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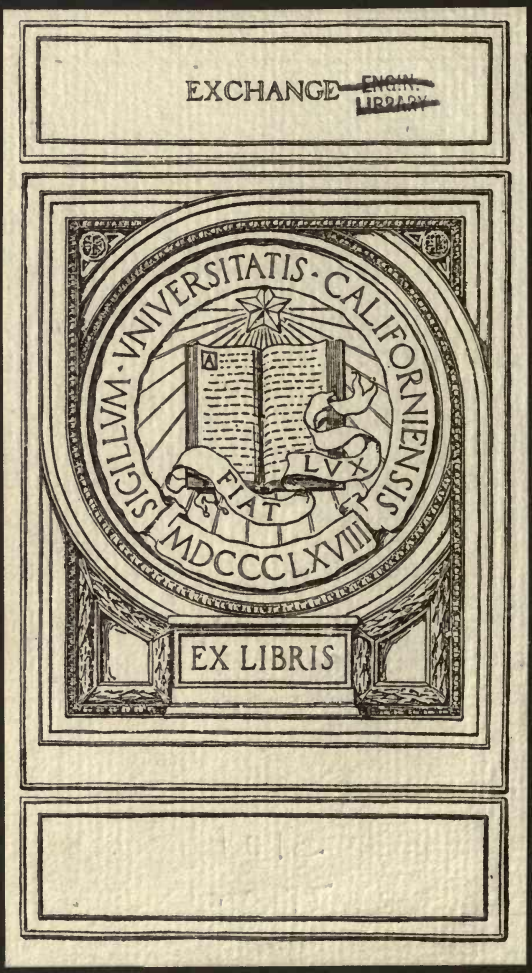

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THERMAL PROPERTIES OF STEAM

BY
G. A. GOODENOUGH

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ENGINEERING EXPERIMENT STATION

BULLETIN NO. 75. SEPTEMBER, 1914

THERMAL PROPERTIES OF STEAM

BY G. A. GOODENOUGH, PROFESSOR OF THERMODYNAMICS.

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THERMAL PROPERTIES OF STEAM.

I. Introduction.

1. *Experimental Data on the Properties of Steam.*—The classic researches of Regnault gave the first reliable knowledge of the properties of steam. Although these experiments were made more than sixty-five years ago (most of Regnault's reports on the properties of steam bear the date 1847) with apparatus and methods incapable of the highest degree of accuracy, they are still deservedly held in high esteem, and until recently, Regnault's data formed the basis of all tabulations of the thermal properties of steam. Within the last ten years there has been a revival of interest in the subject and a number of important investigations, experimental and analytical, have been prosecuted. As a result, we have at present data of a high degree of accuracy covering nearly every phase of the work. The following is a summary of the more important of the experimental investigations:

a. The relation between the pressure and temperature of saturated steam has been established definitely by three series of experiments made respectively by Holborn and Henning, Holborn and Baumann, and Scheel and Heuse. The three series taken together cover the range 32° F. to the critical temperature. These experiments were conducted at the Reichsanstalt with all the resources afforded by modern apparatus and methods of precise measurement.

b. The relation between volume, pressure, and temperature of superheated steam has been determined by the experiments of Knoblauch, Linde, and Klebe at the Munich laboratory. These experiments afford satisfactory data for the range of pressure and superheat covered by them, but an extension over a much wider range should be made.

c. A number of experiments have been made to determine the specific heat of superheated steam. Of these, the experiments conducted in the Munich laboratory, first by Knoblauch and Jakob and afterward by Knoblauch and Mollier, are justly accepted as the most reliable. At the present time similar experiments covering a wider range of pressure are being made by Lanz and Schmidt.

d. The direct experiments of Griffiths, Joly, Smith, Henning, and Dieterici furnish data on the latent heat of saturated steam.

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e. The variation of the specific heat of water has been the subject of several investigations. For the range 32°-212° F. the experiments of Barnes have been verified by those of Callendar, and they are generally accepted. Above 212° F. precise measurements of this important property are lacking. The only available experiments are those of Regnault and Dieterici, and neither of these can be accepted as thoroughly reliable.

f. Four sets of experiments on the throttling of steam by Grindley, Griessmann, Peake, and Dodge, respectively, furnish valuable data that may be used for various purposes. Thus Davis has made effective use of them in establishing the curve of total heat of saturated steam; and in the present investigation they are used as a check on the heat content of superheated steam.

2. *Purpose and Scope of the Investigation.*—The various thermal properties of a vapor are not independent. On the contrary, the equations that express the variations of these properties are related through certain well-known thermodynamic laws. The development of a general theory applicable to a vapor, as water vapor, involves the following steps: 1. The establishment of a system of equations to represent the various thermal magnitudes. The forms of the equations chosen must be such that it is possible by proper selection of arbitrary functions to make the equations satisfy the thermodynamic relations. 2. The comparison of the equations with experimental data and the adjustment of constants to give the best possible agreement. 3. The satisfaction of the various thermodynamic relations. With sufficiently accurate and complete experimental data it should be possible to work out such a theory and thus deduce a set of consistent equations giving all the thermal properties as functions of the independent variables chosen. At the present time the character of the experimental evidence is such as to justify a fresh attack on the problem. It is the purpose of this paper to exhibit the development of a general theory which apparently gives with extreme accuracy the properties of saturated and superheated steam over a range of pressure and temperature far wider than the range covered in technical applications.

In order to make the presentation more useful, and perhaps more intelligible, it has been considered advisable to include (1) a section on thermodynamic relations, and (2) a section devoted to a brief historical review of some of the more important analytical investigations.

3. *Acknowledgment.*—The very considerable labor of computation has been lightened by the assistance of a number of the writer's associates in the Department of Mechanical Engineering. In the earlier phases of the work Mr. A. Schaller and Mr. John A. Dent offered valuable suggestions and cheerfully assumed a considerable part of the work of computation. In the final revision, Mr. S. L. Simmering, fellow in the Engineering College, contributed largely to the progress of the investigation. Mr. G. Meyer, Jr., and Mr. T. E. Maury, senior students, assisted in some of the final computations, and Mr. Meyer made the drawings for the illustrations. The valuable assistance of these men is hereby gratefully acknowledged.

II. Thermodynamic Relations.

4. *Notation.*—Throughout the discussion the following notation is used:

J = mechanical equivalent of heat
$A = 1/J$, reciprocal of mechanical equivalent
t = temperature on F. or C. scale
T = absolute temperature
p = pressure
v = volume of unit weight (1 lb.) of fluid
γ = weight of unit volume
c_v = specific heat at constant volume
c_p = specific heat at constant pressure
u = intrinsic energy per unit weight
q = heat absorbed by fluid per unit weight
q' = heat of liquid
q'' = total heat of saturated steam
i = heat content $= u + Apv$
r = latent heat of vaporization
ρ = internal latent heat
$\psi = Ap\,(v'' - v')$ = external latent heat
s = entropy
μ = Joule-Thomson coefficient

The liquid state is characterized by a symbol with a prime, the state of saturated vapor by the same symbol with a double prime. Thus s', u', and i' denote respectively the entropy, energy, and heat content of the liquid, s'', u'', i'', the same properties of the saturated vapor.

5. *Relations Between Certain Thermal Properties.*—The thermal properties of the liquid and saturated vapor are connected by relations that follow directly from the definition of the properties. Thus

$$r = \rho + \psi = \rho + Ap\,(v'' - v')$$

$$u'' = q' + \rho \qquad q'' = q' + r$$

$$s'' = s' + \frac{r}{T} \qquad i'' = i' + r$$

The heat content i is defined by the relation

$$i = u + Apv$$

u being expressed in thermal units; hence

$$i' = u' + Apv' \qquad i'' = u'' + Apv''.$$

The heat of the liquid is given by

$$q' = \int_{32}^{t} c'dt,$$

in which c' denotes the specific heat of the liquid. If the heat is absorbed by the water at constant atmospheric pressure from 32° to 212°, then for this range

$$q' = i' = \int_{32}^{t} c'dt.$$

The entropy of the liquid is given by

$$s' = \int \frac{dq'}{T} = \int \frac{c'dt}{T},$$

the integral being taken between proper limits.

Above 212° F. a distinction between q'' and i'' must be observed. By definition

$$i'' = u'' + Apv''$$

and $$q'' = u'' + \psi = u'' + Apv'' - Apv'.$$

Hence $$i'' - q'' = Apv',$$

similarly $$i' - q' = Apv'.$$

At low temperatures the difference Apv' is small and negligible. The term *total heat* is often used indiscriminately for q'' and i''; in this discussion, however, total heat refers to q'' and the name *heat content* is reserved for the property denoted by i.

6. *General Equations.*[1]—From the two laws of thermodynamics the following principal equations are deduced.

1. Goodenough's Principles of Thermodynamics, Chap. IV.

$$dq = c_v dT + AT\left(\frac{\partial p}{\partial T}\right)_v dv, \tag{1}$$

$$dq = c_p dT - AT\left(\frac{\partial v}{\partial T}\right)_p dp. \tag{2}$$

The energy equation

$$du = dq - Apdv$$

combined with (1) leads to the fundamental equation

$$du = c_v dT + A\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dv; \tag{3}$$

and the equation of definition

$$di = dq + Avdp$$

combined with (2) gives an analogous equation

$$di = c_p dT - A\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]dp. \tag{4}$$

The application of the criterion of an exact differential to (4) leads to the important Clausius relation

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -AT\left(\frac{\partial^2 v}{\partial T^2}\right)_p. \tag{5}$$

In the case of an isothermal process $dT = 0$ and eq. (4) becomes

$$\left(\frac{di}{dp}\right)_T = -A\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]; \tag{6}$$

while for a throttling process, in which i remains constant, (4) becomes

$$\left(\frac{dT}{dp}\right)_i = \frac{A}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]. \tag{7}$$

The derivative in the first member of (7) is the Joule-Thomson coefficient μ.

At the saturation limit the thermal properties are connected by the Clapeyron-Clausius relation, namely

$$r = AT(v'' - v')\left(\frac{dp}{dt}\right)_{sat}. \tag{8}$$

The derivative $\frac{dp}{dt}$ is obtained from the relation $p = f(t)$ connecting the pressure and temperature of saturated steam.

The relations (5) and (8) are specially important in the development of any general theory of vapors. The equations that express the various thermal properties cannot be developed independently. They are tied together by these relations, which must be satisfied as well as the experimental data.

7. *Development of a General Theory.*—The Clausius relation may be made the basis of a set of equations for a superheated vapor. Let the relation between p, v, and T be given by a characteristic equation

$$v = f(p, T), \tag{9}$$

and let the specific heat c_p at constant pressure, which varies with both pressure and temperature, be expressed by

$$c_p = \phi\,(p, T). \tag{10}$$

Two differentiations of the first equation give the derivative $\frac{\partial^2 v}{\partial T^2}$ and one differentiation of the second equation gives the derivative $\frac{\partial c_p}{\partial p}$. The form of the function in (9) must be so chosen that the experimental measurements of the volume are satisfied, the function ϕ in (10) must likewise satisfy the measurements of specific heat, and furthermore the two functions must satisfy the Clausius relation, $-AT\frac{\partial^2 v}{\partial T^2} = \frac{\partial c_p}{\partial p}$. The development of the theory may proceed along either one of two lines of attack. (1) A charcteristic equation is assumed—this amounts to fixing the function f in (9)—and the constants are determined so as to make the equation represent the volume measurements. Successive differentiation gives the second derivative $\frac{\partial^2 v}{\partial T^2}$, and this is substituted in the Clausius relation. The result is an equation of the form

$$\frac{\partial c_p}{\partial p} = \phi\,(p, T),$$

whence an expression for c_p is found by an integration with respect to p. This will involve an arbitrary function of T as a constant of integration. Finally the equation for c_p is tested by comparison with experimental results. (2) The preceding method may be reversed. Starting with a system of c_p curves laid down from the available experimental evidence, the derivative $\frac{\partial c_p}{\partial p}$ is evaluated, then by two integrations the volume v is determined as a function of p and T.

The first method, which is employed in this investigation, has an inherent difficulty and for that reason has been condemned by Davis and Jakob. It requires the evaluation of the second derivative of an observed magnitude v. Now when a function is empirically fitted to a series of observed values, the errors of the function are liable to be magnified in the first derivative and the second derivative is still more

uncertain. This point may be made clearer by a geometrical illustration. If the experimental points are plotted on the v, T plane in groups, each representing a constant pressure, a series of curves may be made to pass through the groups of points with reasonable accuracy. The second derivative $\frac{\partial^2 v}{\partial T^2}$ measures the curvature of these constant-pressure lines, hence the curves must not only fit the observed values of v, but they must have precisely the proper curvature.

The second method has been used by Jakob in his investigation (see p. 14). Its chief disadvantage is the practical difficulty of performing the mathematical operations involved. Jakob avoided this difficulty by the use of graphical methods, and his results were thus obtained by the measurement of lines and areas. Herein lies the advantage of the first method if it can be successfully applied. The mathematical manipulation is simple and direct, the various thermal magnitudes are given by closed expressions and therefore they may be calculated without recourse to measurement or approximation.

With the expressions for v and c_p established by either method, an equation for the heat content i is found upon substituting these expressions in the general equation (4). A similar substitution in the general equation (2) leads to an equation for the entropy. The heat content equation when applied at the saturation limit must give values that satisfy the Clapeyron relation, eq. (8). Another check on the i equation is furnished by the various sets of throttling experiments. According to thermodynamic theory the heat content i remains constant in a throttling process; hence the constant-i lines deduced from the equation for i should lie in close coincidence with the experimental points.

III. Review of Earlier Investigations.

8. *Zeuner's Theory.*—In this section is given a brief review of the more important theoretical investigations on the thermal properties of steam. Aside from historical interest, such a review is valuable in showing the development of the analytical processes with increasing experimental evidence; and also in exhibiting the various methods of attacking the problem.

The starting point of Zeuner's investigation[1] is the assumption of a characteristic equation for superheated steam of the form

$$pv = BT - R,$$

1. Zeuner's Technical Thermodynamics, Klein's Tr., Vol. II, pp. 229-243.

in which the correction term R is considered to be a function of the pressure p only. Following Regnault's experiments, the specific heat c_p is taken as a constant, viz. $c_p = 0.4805$. Then from the fundamental equations of thermodynamics, the law governing the adiabatic expansion of superheated steam is deduced in the form

$$\frac{T}{T_1} = \left(\frac{p}{p_1}\right)^m$$

which is the form found for adiabatic expansion of a gas, provided

$$m = \frac{k-1}{k} .$$

By a comparison of two expressions for the entropy of saturated steam the constant m is given the value 0.25. The correction term R is taken proportional to the fourth root of the pressure, and the characteristic equation thereupon becomes

$$pv = BT - Cp^{\frac{1}{4}}.$$

The energy and heat content of unit weight of saturated steam are given respectively by the simple expressions

$$u = u_o + \frac{Apv}{k-1}$$

$$i = u_o + \frac{k}{k-1} Apv,$$

and with $k = \frac{4}{3}$, these become, in English units,

$$u = 857 + 3\,Apv$$
$$i = 857 + 4\,Apv.$$

Zeuner compared the saturation volumes deduced from the characteristic equation with those given in Regnault's tables and found excellent agreement. The volumes of the superheated vapor deduced from the equation were compared with a few experimental values given by Hirn and Battelli and fair agreement was observed. The heat content of the saturated vapor calculated from the formula for i checked with the values derived from Regnault's formula.

Zeuner's theory represented excellently the experimental evidence available at the time it was presented. The Munich experiments, however, have shown conclusively (1) that the form of the characteristic equation assumed by Zeuner cannot possibly represent correctly the volume measurements; (2) that the specific heat c_p is not a constant but a function of both the temperature and pressure. Furthermore, the admirable investigation of Davis has shown that Regnault's linear

formula for the heat content is clearly in error. The foundations of Zeuner's theory are therefore torn away.

9. *Callendar's Theory*[1].—The theory proposed by Callendar is assumed to apply to all vapors. The starting point of the investigation is a modification of the Joule-Thomson equation

$$v = \frac{BT}{p} - \frac{a}{BT^2}$$

Callendar observes (1) that the equation of a perfect gas at high temperatures is not $pv = BT$, but $p(v-b) = BT$, where b is the minimum volume or "co-volume" of Hirn and van der Waals. The value of b may probably be taken as equal to the volume of the liquid when the vapor pressure is small. (2) If it be assumed that the average total kinetic energy of the molecules of a gas is directly proportional to the energy of translation, then the limiting value of the specific heat of a gas in the ideal state ($p = 0$, $v = \infty$) either at constant pressure or at constant volume must be constant. It is further assumed that the kinetic energy of the vapor is proportional to $p(v-b)$ at all stages. Then the exponent of T in the small correction term $\frac{a}{BT^2}$ of the Joule-Thomson equation is not 2 but $n = \frac{(c_v)_o}{B}$, the ratio of the limiting value of the specific heat at constant volume to the limiting value of pv/T. Next adopting the hypothesis of Maxwell regarding the partition of energy, the limiting value of this ratio for a triatomic gas like steam or CO_2 should be 3.5. The equation deduced from these considerations is

$$v - b = \frac{BT}{p} - c_o\left(\frac{T_o}{T}\right)^{3.5},$$

in which T_o denotes the absolute temperature corresponding to 0° C. (273.1 C. or 459.6 F.). Taking $c_o T_o^{3.5}$ as a single constant m, the equation becomes

$$v - b = \frac{BT}{p} - \frac{m}{T^{3.5}}.$$

By the application of the Clausius relation, the specific heat at constant pressure is given by the expression

$$c_p = (c_p)_o + \frac{Amn\,(n+1)}{T^{4.5}}$$

in which $(c_p)_o$ denotes the assumed constant limiting value of c_p when

1. On the Thermodynamical Properties of Gases and Vapors. Proc. of the Royal Soc. of London, Vol. 67 (1900), pp. 266-286.

$p = 0$. Expressions for heat content, energy, and entropy are readily derived. The value of the constant $(c_p)_o$ is given as 0.4966, and with this Callendar computed values of c_p at the saturation limit for the range 0°–200° C. Values of the total heat, latent heat, and entropy for the same range were also computed and tabulated.

Callendar's work was published in 1900, five years before the appearance of the Munich experiments and eight years before the publication of Davis' work on the total heat of steam. It is interesting to note that Callendar, on purely theoretical grounds, and in opposition to the then existing experimental evidence, forecast the more important of the recent developments of the subject. He showed the variation of the specific heat with pressure and temperature, though the values he calculated are not in good agreement with those now generally accepted. He challenged the accuracy of Regnault's linear equation for total heat and predicted the proper form of the total heat curve, as it was afterward established by Davis. He calculated from Joly's experiments the value of the latent heat at 100° C. (212° F.) as 540.2 Cal., almost exactly the value that is now considered most probable. Upon the appearance of the Munich volume measurements it was found that Callendar's characteristic equation represented them quite accurately up to 160° C. Above 160° the agreement was not so good for the reason that the equation gives the isotherms on the pv–p plane as straight lines, while the experimental points indicated isotherms with an appreciable curvature.

The fundamental defect in Callendar's theory is the assumption of the constancy of the specific heat $(c_p)_o$ at zero pressure. In the absence of experimental evidence the assumption was natural and the basis for it appeared plausible. The experiments of Knoblauch and Jakob and the later confirmatory experiments of Knoblauch and Mollier showed conclusively that $(c_p)_o$ cannot possibly be a constant. The same thing is shown by the specific heat measurements of Mallard and Le Chatelier and of Langen at very high temperatures.

Callendar's paper is properly regarded as one of the most important of the contributions to the literature on the properties of vapors. It contains suggestions of the highest value, and it shows what may be accomplished by the application of pure theory. However, in the light of the experimental evidence accumulated since the publication of the paper, it is clear that Callendar's equations without modification should not at present be used as a basis for a tabulation of steam properties.

Professor Mollier of Dresden, recognizing the importance of Callendar's investigation, made it the basis of a set of steam tables pub-

lished in 1906.[1] The work of Mollier has been practically duplicated by Smith and Warren[2] in their new steam tables published in 1912. It is difficult to justify the appearance of the last set of tables. The authors make a claim for the consistency of the values, a claim which is readily granted since the values were calculated from a set of equations properly related through the general thermodynamic equations. Consistency is obtained, however, at the expense of accuracy. No account whatever is taken of the Munich experiments on specific heat and even Barnes' noteworthy experiments on the specific heat of water are neglected. The Mollier and the Smith and Warren tables are doubtless much better than the older tables based entirely on Regnault's data; but on the score of accuracy, they are not to be compared with the Marks and Davis tables or with Peabody's latest tables.

10. *Davis' Investigations.*—To Dr. H. N. Davis of Harvard University we are indebted for two of the most valuable and important contributions to the literature of the properties of steam.

In his first paper,[3] Dr. Davis investigated the Joule-Thomson effect in the case of steam, using for this purpose the throttling experiments of Grindley, Griessmann, Peake, and Dodge. The object of the investigation was the verification of the law of corresponding states. From the four sets of throttling experiments, values of the Joule-Thomson co-efficient μ were determined, and the "reduced" values of μ were compared with values of μ for carbon dioxide. It was found that the law was verified within the limit of error of the experiments. With respect to the properties of steam, the most useful result of the investigation was the establishment of a curve showing the variation of μ with the temperature.

The important feature of Davis' second paper[4] is the discussion of the new formula for the heat content of saturated steam. The throttling experiments were undertaken primarily for the purpose of gaining information on the specific heat of superheated steam. All attempts along this line were unsuccessful for the reason that the calculated specific heat depends upon the *rate* of variation of the heat content, and consequently errors in the formula for heat content are enormously magnified in the calculated values of the specific heat. Grindley and Griessmann used Regnault's linear formula for heat content and were

1. Neue Tabellen und Diagramme für Wasserdampf. Berlin. 1906.
2. The New Steam Tables, D. Van Nostrand Co., N. Y. 1912.
3. On the Applicability of the Law of Corresponding States to the Joule-Thomson Effect in Water and Carbon Dioxide. Proc. Am. Acad. Arts & Sciences, Vol. 45, pp. 243-264.
4. Notes on Thermal Properties of Steam. Proc. Am. Acad., Vol. 45, pp. 267-311, 1900. See also Proc. A. S. M. E., Vol. 30, p. 1419, 1908.

unable to obtain any consistent results. When the calculation is reversed, that is, when the variation of i is determined from the assumed values of c_p, errors in c_p are reduced in the calculation of i. The experiments of Knoblauch and Jakob give reliable values of c_p. With these available, Davis conceived the possibility of reversing the method. Taking the two sets of experimental data (1) the throttling experiments, (2) the Knoblauch values of c_p, he deduced his well-known formula

$$i'' = i_{212} + 0.3745\ (t - 212) - 0.00055\ (t - 212)^2$$

which is universally accepted for the temperature range 212°–400° F. That the Regnault linear formula for heat content was inexact had been apparent for some time; in fact, Callendar in 1900 had called attention to the matter, and from his theory had obtained an i-curve differing materially from Regnault's straight line. The achievement of Davis in definitely settling this vexed question must be regarded as one of the most noteworthy in the history of the subject.

A section of the paper is devoted to a critical discussion of the specific heat of superheated steam, and the results of the researches of the Joule-Thomson effect are used to develop important relations between the specific heat and the coefficient μ. (See p. 36.)

Davis also discusses the test furnished by the Clausius relation (page 8) and points out that Linde's characteristic equation can not be reconciled with the Knoblauch specific heat measurements through this relation. He goes so far as to say that such reconciliation is impossible, taking the accepted volume and specific heat measurements.

The investigations of Davis are embodied in the Marks and Davis steam tables.

11. *Jakob's Investigation.*[1]—The Clausius relation is taken as the basis of the investigation, but the method used is the reverse of that used in the development of the present theory. Jakob first lays down a system of c_p-curves in accordance with the experiments of Knoblauch and Jakob and Knoblauch and Mollier. In the adjustment of the curves use is made of the thermodynamic relation suggested by Davis (see p. 36). The characteristic equation is given the form

$$v = \frac{BT}{p} - R,$$

in which the correction term R is a function of p and T. Since

$$-\frac{\partial^2 v}{\partial T^2} = \frac{\partial^2 R}{\partial T^2}$$

1. Zeit. des Verein. deutsch. Ing., Vol. 56, pp. 1980-1988. 1912.

the Clausius relation gives

$$\left(\frac{\partial c_p}{\partial p}\right)_T = AT\frac{\partial^2 R}{\partial T^2},$$

whence

$$R = \frac{1}{A}\int\int\frac{1}{T}\frac{\partial c_p}{\partial p}dt^2.$$

To obtain a lower integration limit, Jakob attempts to set a value of T at which temperature the derivative $\frac{\partial c_p}{\partial p}$ reduces to zero. By a rather arbitrary process he arrives at the value of $T = 1200°$ C., approximately. Hence at this temperature the term R changes sign. No attempt is made to deduce an equation $c_p = \phi\ (p, T)$, and consequently the integrations required in the determination of R are performed graphically. The final result of the process is a set of values of the specific volume v, which are compared with the volumes calculated from Linde's equation.

Jakob also gives a tabulation of the heat content of superheated steam. From the assumed specific heat curves, the mean specific heat from saturation to a given temperature t is obtained by measurement; the product $c_{pm}\ (t - t_s)$ then gives the heat absorbed during superheat, and the sum $i_{sat} + c_{pm}\ (t - t_s)$ is the required value of i.

12. *Heck's Theory.*—Professor R. C. H. Heck has published several papers on the properties of steam, and in his latest paper[1] he has developed a complete theory.

The starting point of Heck's investigation is the Joule-Thomson effect. Taking the identity

$$\left(\frac{\partial i}{\partial p}\right)_t = -\left(\frac{\partial i}{\partial t}\right)_p\left(\frac{\partial t}{\partial p}\right)_i = -c_p\,\mu,$$

the variation of μ with the temperature is known at least approximately from the work of Davis. A relation between i and p with t constant is thus determined, and ultimately an equation for i is deduced. This has the form

$$i = i_o + y'p + z'p^{2.4}$$

in which i_o, y' and z' are rather complicated functions of the temperature. The function i_o is the heat content for $p = 0$. To get this the specific heat c_{po} for $p = 0$ has to be determined, and for this purpose

1. Journal A. S. M. E., Nov. 1913, pp. 1619-1630.

the Knoblauch and Mollier experiments are used. The equation for c_{po} is

$$c_{po} = 0.302 + \frac{114.66}{t + 688} + 0.000144t.$$

The general equation (6), p. 7, now furnishes a relation from which the form of the characteristic equation may be inferred. That this relation may be satisfied it is sufficient to give the characteristic equation the form

$$pv = BT - yp - zp^{2.4}$$

in which y and z are functions of t that are related respectively to the functions y' *and* z'. The constants in the various functions are so adjusted that the i and v equations satisfy the Clausius relation, and at saturation the Clapeyron relation.

Heck's theory satisfies all the requirements imposed by thermodynamic laws. Unfortunately, the paper was published in abstract and the most valuable part—the comparison of the theory with experimental data—was omitted. It may safely be assumed, however, that the agreement is satisfactory.

13. *Other Investigations.*—Other investigations of less immediate importance may be noted.

Linde[1] in his discussion of the experiments of the Knoblauch, Linde, and Klebe experiments, after establishing his two characteristic equations, attempted to deduce from them the latent heat of steam and the specific heat of superheated steam. The results obtained were not confirmed by the later experiments on specific heats.

Dieterici's paper entitled "Energieisothermen des Wassers bei hohen Temperaturen"[2] describes an attack on the problem of the properties of steam by an original and ingenious method. In the light of our present knowledge, some of the basic assumptions are unsound, and the results therefore have no significance.

Schüle[3] has recently published a tabulation of steam properties. The values were obtained by purely empirical processes, and no attempt was made to correlate them through thermodynamic relations. Perhaps the most valuable part of Schüle's work is the attempt to determine the properties in the vicinity of the critical temperature.

1. Mitteil. uber Forschungsarbeiten, Vol. 21, pp. 57-92.
2. Annalen der Physik (4), Vol. 16, pp. 907-930.
3. Zeit. des Verein. deutsch. Ing., Vol. 55, pp. 1506-1512, 1561-1567.

IV. Development of a General Theory of the Properties of Steam.

14. *Units and Constants Employed.*—In this section is given the development of the equations that represent the various properties of saturated and superheated steam. The order of topics is as follows:

A. Relation between pressure and temperature of saturated steam.
B. Specific volumes. Characteristic equation of superheated steam.
C. Specific heat of superheated steam.
D. Heat content, latent heat, heat of liquid, energy, and entropy.
E. The Joule-Thomson effect.
F. Thermal properties near the critical temperature.

As a preliminary step, the establishment of certain units and constants is necessary. These are

1. The thermal unit.
2. The mechanical equivalent of heat.
3. The temperature of melting ice on the absolute scale.

In this investigation the mean B.t.u. is taken as the thermal unit. This is defined as 1/180th of the heat required to raise the temperature of a pound of water from 32° to 212° F. The corresponding mean calorie is by Griffiths[1] identified with the 17½° calorie and by Barnes with the 16° calorie.

The various determinations of the mechanical equivalent seem to justify the value established by Griffiths[1] in 1893, namely,

$$1 \text{ mean calorie} = 4.184 \text{ joules}$$
$$1 \text{ mean B.t.u.} = 777.64 \text{ standard ft. lb.}$$

This value has been used.

Various determinations of the absolute temperature of the ice-point are discussed by Marks and Davis[2], and the value chosen by them is 491.°64. It does not seem that the evidence is sufficient to justify the degree of accuracy indicated by the fifth figure; hence in this investigation 491.°6 has been used. The relation between absolute and ordinary temperatures is thus given by

$$T = t + 459.6.$$

A. Relation between Temperature and Pressure of Saturated Steam.

15. *Experimental Data.*—The important relation $p = f(t)$ for saturated steam has been definitely determined by three sets of experi-

1. The Thermal Measurement of Energy.
2. Steam Tables, p. 88.

ments conducted at the Reichsanstalt within the last five years. Each set covers a different range of temperature; Scheel and Heuse's[1] experiments cover the lower range 0–50° C. (32°–122° F.), Holborn and Henning's[2] the range 50°–200° C. (122°–392° F.), while Holborn and Baumann's[3] experiments extend from 200° to the critical temperature. The character of the work done at the Reichsanstalt is a sufficient guaranty that every precaution was taken and that the measurements are as precise as can be obtained with modern instruments and methods.

The values of the saturation pressure as deduced from the respective sets of experiments are given in the following tables. In the third table the values are not those given by Holborn and Baumann but values deduced therefrom by Prof. Marks.[4]

TABLE 1.

SCHEEL AND HEUSE.

Temp. C.	Pressure in mm. of mercury									
	0	1	2	3	4	5	6	7	8	9
0	4.579	4.926	5.254	5.685	6.101	6.543	7.014	7.514	8.046	8.610
10	9.210	9.845	10.519	11.233	11.989	12.790	13.637	14.533	15.840	16.481
20	17.539	18.655	19.832	21.074	22.383	23.763	25.217	26.747	28.558	30.052
30	31.834	33.706	35.674	37.741	39.911	42.188	44.577	47.082	49.708	52.459
40	55.341	58.36	61.52	64.82	68.28	71.90	75.67	79.62	83.74	88.05
50	92.54									

TABLE 2.

HOLBORN AND HENNING.

Temp. C.	Pressure in mm. of mercury				
	0	2	4	6	8
50	92.3	101.9	112.3	123.6	135.9
60	149.2	163.6	179.1	195.9	214.0
70	233.5	254.5	277.1	301.3	327.2
80	355.1	384.9	416.7	450.8	487.1
90	525.8	567.1	611.0	657.7	707.3
100	760.0	815.9	875.1	937.9	1004
110	1074.5	1149	1227	1310	1397
120	1489	1586	1687	1795	1907
130	2026	2150	2280	2416	2560
140	2709	2866	3030	3202	3381
150	3569	3764	3968	4181	4402
160	4633	4874	5124	5384	5655
170	5937	6229	6533	6848	7175
180	7514	7866	8230	8608	8999
190	9404	9823	10256	10705	11168
200	11647	12142	12653		

1. Annalen der Physik (4), Vol. 31, pp. 715-735, 1910.
2. Annalen der Physik (4), Vol. 25, pp. 833-883, 1908.
3. Annalen der Physik (4), Vol. 31, pp. 945-970, 1910. See also articles by Risteen; The Locomotive, Vol. 26, pp. 85, 183, 246; Vol. 27, p. 54; Vol. 28, pp. 88, 118.
4. Proc. A. S. M. E., Vol. 33, p. 572.

TABLE 3.

HOLBORN AND BAUMANN.

Temp. F.	Pressure in lb. per sq. in.									
	0	10	20	30	40	50	60	70	80	90
400	246.99	276.34	308.33	343.18	380.92	421.85	465.95	513.65	565.08	620.18
500	679.26	742.55	810.31	882.58	959.85	1042.2	1130.2	1223.7	1323.0	1428.3
600	1539.9	1657.8	1782.9	1915.3	2055.1	2203.1	2359.2	2523.4	2697.1	2882.3
700	3083.4									

16. *Pressure-Temperature Formulas.*—A large number of formulas have been proposed to represent the relation between pressure and temperature of saturated steam. The greater number of these are purely empirical, but a few have a semi-rational basis.

Of the earlier formulas suggested, two have been quite generally used, namely, Roche's and Biot's.[1] From certain theoretical considerations Roche deduced the form

$$p = a\, a^{\frac{\theta}{m+n\theta}}$$

in which a, a, m, and n are constants and $\theta = t + \text{const.}$, that is, θ denotes the temperature measured from some zero arbitrarily chosen. Biot suggested the more general form.

$$\log p = a + ba^{\theta} + c\beta^{\theta}$$

which has five constants. The Biot formula has been generally used to represent Regnault's experiments.

A group of formulas may be deduced from the following considerations. The Clapeyron relation

$$r = AT\,(v'' - v')\,\frac{dp}{dt}$$

may be written in the form

$$\frac{dp}{p} = \frac{1}{T}\,\frac{r}{Ap\,(v'' - v')}dT.$$

In the fraction of the second term the numerator is the latent heat r and the denominator is the external latent heat,

$$\psi = Ap\,(v'' - v')$$

that is, the part of r that is used in overcoming external resistance. If values of r and of ψ be plotted as ordinates against temperatures as abscissas, the resulting curves are of such character that they can be represented very closely by equations of the type

1. Preston's Theory of Heat, Art. 188.

$$r = a_1 + a_2T + a_3T^2 + a_4T^3 + \ldots\ldots$$
$$\psi = T\,(b_1 + b_2T + b_3T^2 + b_4T^3 + \ldots\ldots)$$

The second curve should properly pass through the origin, since the product pv'' should approach zero as T approaches zero. By division

$$\frac{r}{\psi} = \frac{1}{T}\,(c_1 + c_2T + c_3T^2 + c_4T^3 + \ldots\ldots)$$

and the substitution of this expression in the original Clapeyron relation leads to the differential equation

$$\frac{dp}{p} = \frac{1}{T^2}\,(c_1 + c_2T + c_3T^2 + c_4T^3 + \ldots\ldots)\,dT.$$

The integration of this equation gives the following general form for the relation $p = f(t)$

$$\log p = A + \frac{B}{T} + C \log T + DT + ET^2 + FT^3 + \ldots\ldots \qquad (11)$$

The number of constants may be increased indefinitely by taking more terms involving the higher powers of T; hence the equation may be fitted if desired to a large number of experimental points. The signs of the coefficients B, C, D, E, etc., may, of course, be either positive or negative.

Several formulas that have been proposed are simply modifications of this general equation.

a. The *Dupré-Hertz formula,* which is usually written in the form

$$\log p = k - m \log T - \frac{n}{T},$$

includes the first three terms of the general equation.

b. Callendar's formula.[1]—Callendar deduced from his equations for total heat and entropy a pressure-temperature relation of complicated form, but remarked that the equation could be written in the form

$$\log p = A + \frac{B}{T} + C \log T + \text{small terms.}$$

c. Bertrand's formulas.[2]—If the expressions for r and $Ap\,(v'' - v')$ are taken as linear in T, the integrand assumes a form that permits integration in finite terms. Bertrand assumed that for water vapor the following relations are sufficiently well satisfied.

$$p\,(v'' - v') = B\,(T + a), \quad r = M - nT$$

The Clapeyron relation then becomes

$$\frac{dp}{p} = \frac{m - nT}{ABT\,(T + a)}\,dT$$

1. Proc. Royal Soc. of London, Vol. 67, p. 285, 1900.
2. Chwolson, Lehrbuch der Physik, Vol. 3, p. 736.

from which $$p = k \frac{T^a}{(T+a)^\beta}$$

or $$\log p = \log k + a \log T - \beta \log (T+a)$$

In deducing Bertrand's second formula, it is assumed that the relation

$$\frac{Ap\,(v''-v')}{r} = aT - b$$

holds good for steam. From this relation the equation

$$p = k \left(\frac{T-m}{T}\right)^n$$

or $$\log p = \log k - n \log \frac{T}{T-m}$$

is easily obtained. While Bertrand's equations are convenient for the purposes of calculation, they cannot be extended over any considerable temperature range without change of constants. The same statement applies to the Dupré-Hertz formula.

d. Marks' formula.—If in the general equation (11) the constant C is made equal to zero and terms containing powers of T above the second are suppressed, the resulting equation has the form deduced from quite different considerations by Prof. Marks.[1]

One other formula should be mentioned. Thiesen's formula involves the critical temperature t_k and atmospheric pressure. In the metric units (p in mm. of mercury and t in deg. C.) it may be written in the form

$$T \log \frac{p}{760} = A\,(t-100) - B\,(t_k - t)^4 - (t_k - 100)^4$$

Thiesen's formula is used as a standard of reference by Henning[2] in an elaborate discussion of various pressure-temperature measurements.

It is an easy task to fit any of the proposed equations to the experimental values through a limited temperature range; but to obtain a single equation that will satisfactorily represent the experiments over the entire range from 32° to the critical temperature is a problem of some difficulty.

Marks' equation,

$$\log p = A - \frac{B}{T} - CT + DT^2,$$

represents the experimental values above 400° F. with remarkable accu-

1. Proc. A. S. M. E., Vol. 33, p. 573.
2. Annalen der Physik (4), Vol. 22, pp. 609-630, 1907.

racy and may be extended to 300° F. with satisfactory results. Below 300° the Marks curve begins to run below the experimental points, as shown in Fig. 1, and the Scheel and Heuse points are missed entirely. Heck[1] has slightly changed the constants of the Marks equation with the avowed purpose of getting the proper value of p at 212° F. At this temperature the Marks equation gives $p = 14.672$, while the exact value is 14.697. The two sets of constants are as follows:

	Marks	Heck
$A =$	10.515345	10.606400
$\log B =$	3.6878597	3.6897500
$\log C =$	$\bar{3}$.6075880	$\bar{3}$.6205462
$\log D =$	$\bar{6}$.1439400	$\bar{6}$.1601803

$$T = t + 459.64$$

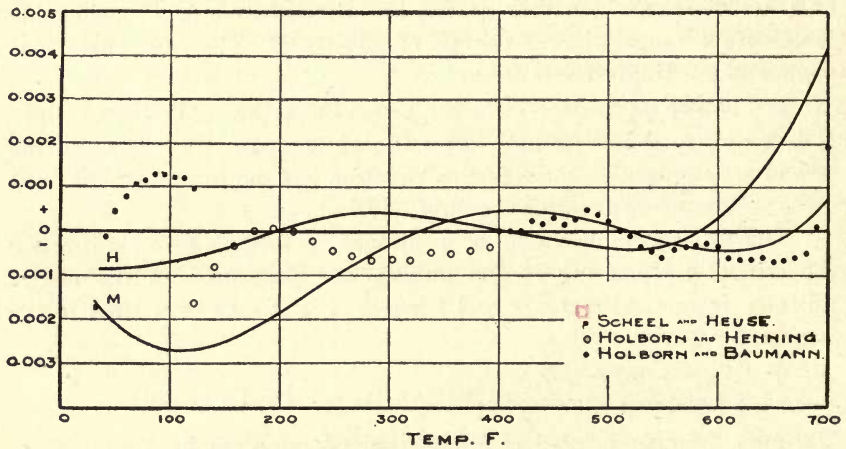

FIG. 1. PRESSURE AND TEMPERATURE OF SATURATED STEAM.

The curve H, Fig. 1, shows the agreement between Heck's equation and the experimental points. It is apparent that Heck's modification improves the agreement throughout the lower range of temperature, which is the most important. Above 600°, however, Heck's curve begins to deviate widely from the Holborn and Baumann points.

The equation worked out in the present investigation may in a sense be regarded as a modification of Marks' equation. In the first place a term involving $\log T$ was added as is suggested by the general form (11). The equation thus took the form

1. Journal A. S. M. E., Vol. 35, p. 1627, 1913.

$$\log p = A - \frac{B}{T} - C \log T - DT + ET^2,$$

and the following constants were determined:

$A = 10.5688080$	$\log D = \bar{3}.6088020$
$\log B = 3.6881209$	$\log E = \bar{6}.1463000$
$C = 0.0155$	$T = t + 459.6$

With these constants, the equation represents the Holborn and Baumann points above 400° with substantially the same accuracy as the Marks equation, and it represents the experiments throughout the range 32°–300° very much better than the Marks equation. It is, however, open to two objections: (1) At 212° it gives $p = 14.694$, which is still too low; (2) at 32° it gives a value of p considerably higher than is indicated by the Scheel and Heuse experiments.

It was found that these objections could be removed and the agreement improved throughout by the inclusion of a small correction term. The final equation is, therefore,

$$\log p = A - \frac{B}{T} - C \log T - DT + ET^2 - \Delta \qquad (A)$$

where $$\Delta = 0.0002\ (10 - 10\,\theta^2 + \theta^4),$$

and $$\theta = \frac{t - 370}{100}.$$

The addition of the term Δ amounts to the inclusion of terms involving T^3 and T^4 in the general formula (11). The values of $C \log T$ and Δ are easily calculated, and since Δ is an even function of t the values below 370° are duplicated above 370°. The labor of calculation is therefore not materially increased by the inclusion of these terms.

17. *Comparison of Formulas.*—In Fig. 1, equation (A) is used as a standard of reference. The points plotted are taken from the preceding tables, and the curves M and H represent respectively the equations of Marks and Heck. Ordinates represent the relative deviation from the value of p calculated from the formula. It is seen that the proposed equation (A) represents the experimental values with a high degree of accuracy. The deviations except at two or three isolated points are well within 1 part of 1000, which is probably within the limit of accuracy of the experiments. For the lower range 32° to 400°, Heck's formula is superior to Marks', and the proposed formula (A) is superior to both. Above 450° Marks' formula gives slightly better results than the new formula, and Heck's equation shows considerable deviation from the experimental points.

It will be seen that none of the three curves follows the general course of the Scheel and Heuse points. Both the M and H curves tend to favor the low Holborn and Henning point at 122° F. rather than the high Scheel and Heuse point at the same temperature. The curve of equation (A) on the other hand, lies nearer the Scheel and Heuse points throughout except at the extreme end of the range near 32°. The discrepancy between the two points at 122° is greatly magnified in the figure; the actual pressure difference is 0.24 mm. of mercury. Scheel and Heuse have noted this discrepancy and they defend the higher point. Equation (A) is probably more accurate throughout the range 40°–200° than either of the others. At 32° the value calculated from the equation is 4.587 mm. while the accepted value is 4.579 mm. of mercury. The discrepancy is unimportant so far as pressures are concerned. The significant fact is that, accepting the Scheel and Heuse points as authentic, the derivative $\frac{dp}{dT}$ calculated from any one of the three of the equations must be too small in the range 32°–80°. The effect of this error will be shown in another section.

B. VOLUME OF SUPERHEATED AND SATURATED STEAM. CHARACTERISTIC EQUATIONS.

18. *Experimental Data.*—Direct experiments on the specific volume of saturated and superheated steam have been made by Ramsay and Young[1], by Battelli[2], and by Knoblauch, Linde, and Klebe[3]. The experiments in the Munich laboratory conducted by Knoblauch, Linde, and Klebe were so superior in all respects to those of the other investigators, that the results are generally accepted as decisive.

The apparatus used in the Munich experiments was so arranged that three sets of observations were made. 1. The pressure of the saturated vapor corresponding to the temperature. 2. Simultaneous values of pressure and temperature corresponding to a predetermined constant volume of superheated steam. 3. The corresponding saturation values of p and t for the given volume. In conducting the experiment the volume of a predetermined weight of steam was kept constant and corresponding temperatures and pressures were observed. These observed values of p and t when plotted give a constant volume curve, or "isochor" on the pt-plane. It was found that the curves, within the limits of accuracy of the experiments, were straight lines. These lines were

1. Phil. Trans. Roy. Soc. of London, Vol. 183-A, p. 107 (1892).
2. Annales de Chimie et de Physique (7), Vol. 3, p. 408 (1894).
3. Mitteilungen über Forschungsarbeit., Vol. 21, pp. 33-72 (1905).

prolonged to intersect the saturation curve $p = f(t)$, and the points of intersection gave, therefore, simultaneous values of p, v, and t, at the saturation limit.

For convenience in establishing a characteristic equation, Linde made use of the scheme of representation devised by Amagat. Values of the product pv were plotted as ordinates against values of p as abscissas. The experimental points were not taken for this purpose but rather the points determined by the intersection of the successive isochors by lines of constant temperature. In this way the points on the pv-p plane are separated into groups, each of which is associated with a particular temperature. In other words, curves through the successive sets of points are lines of constant temperature, or isotherms. Fig. 2 shows the points as thus determined. These were not copied from Linde's chart, but were calculated independently from the experimental data by Mr. Simmering.

19. *Characteristic Equations.*—A large number of equations have been proposed to represent the relation between the p, v, and t of superheated vapors. In general these equations have the form

$$pv = BT - R$$

or the form

$$p(v - b) = BT - R,$$

in which R is the so-called *correction term.* In the second form account is taken of the co-volume (see p. 11). The term R is taken as a function of one or more of the variables, p, v, t. Zeuner makes $R = Cp^{\frac{1}{4}}$, Tumlirz assumes simply $R = Cp$. In Callendar's equation, namely

$$p\,(v - b) = BT - pc_0 \left(\frac{T_0}{T}\right)^{-3.5}$$

R is proportional to the product $pT^{-3.5}$. It may be noted that if R is taken as a function of p and T, or as a function of p alone, and p appears in the first power only, then the isothermals on the pv-p plane are straight lines. The Tumlirz equation $pv = BT - cp$ gives a group of parallel straight lines, while the Callendar formula gives straight lines inclined at different angles. In one group of equations the term R is made a function of v alone or a function of v and t. In the well known van der Waals equation

$$R = C\frac{v - b}{v^2},$$

and in the Clausius equation

$$R = \frac{C}{T}\frac{v - a}{(v + B)^2}.$$

In the first empirical formula proposed by Linde

$$R = \frac{1}{v}\left[C\left(\frac{373}{T^2}\right) - D\right].$$

Since p and T are always taken as the independent variables and v is the magnitude calculated, it is extremely inconvenient to have an equation with a power of v higher than the first; hence equations having R a function of p and T have a practical advantage. With this point in view, Linde constructed his second equation, namely

$$pv = BT - p\,(1 + ap)\left[C\left(\frac{373}{T}\right)^3 - D\right].$$

This equation has been generally accepted, and from it have been calculated the values of v that appear in the Marks and Davis and the Peabody steam tables.[1]

While Linde's second equation represents the experiments within the limits of accuracy it is open to two serious objections. (1) At 402° C. the correction term R vanishes and for higher temperatures it changes sign. In the language of Linde, the vapor bcomes a more than perfect (übervollkomenes) gas at temperatures above 402°. (2) Taking the specific heat measurements of Knoblauch and Mollier as decisive, it is impossible to satisfy the Clausius thermodynamic relation with the values of the derivative $\frac{\partial^2 v}{\partial T^2}$ obtained from Linde's equation. This means that while the constant pressure curves deduced from Linde's equation pass through the experimental points with sufficient accuracy, they have not the proper curvature. Dr. Davis in his paper on the properties of steam[2] has pointed out this defect, and has expressed the opinion that no reliable c_p values can be obtained through the Clausius equation from any volume measurements as yet available. That this view is not justified will be shown in the following section.

In the course of the present investigation a number of equations have been developed. These differ slightly in form, and each may be considered a modification of Linde's second equation. The first equation[3] was given the form

$$v + c = \frac{BT}{p} - (1 + ap)\,\frac{m}{T^n}.$$

1. Marks and Davis, Steam Tables and Diagrams, p. 98.
2. Am. Acad. of Arts and Sciences, Vol. 45, p. 288 and p. 303.
3. Goodenough's Principles of Thermodynamics, p. 203.

The equation resembles Linde's equation in retaining the expression $(1+ap)$ which serves to give the parabolic form to the isothermals when drawn in the pv-p plane. See Fig. 2. The constant D in Linde's equation is dropped, but another constant is added to v. The values assigned to the constants were as follows:

Metric units (p in kg. per sq. m.)	English units (p in lb. per sq. in.)
$B = 47.113$	$B = 0.5963$
$\log m = 11.19839$	$\log m = 13.67938$
$n = 5$	$n = 5$
$c = 0.0055$	$c = 0.088$
$a = 0.00000085$	$a = 0.0006$

With these constants the equation represents the experimental results with substantially the same accuracy as Linde's equation; and by means of the Clausius relation the specific heat measurements of Knoblauch and Mollier are fairly well verified.

A careful study of conditions to be satisfied led to further modifications. It was found that more consistent results could be obtained by taking a fractional power of p in the correction term. Further, it was found that by taking 4 instead of 5 for the exponent n the constant c could be omitted. Hence the second equation was given the form

$$v = \frac{BT}{p} - (1 + 3ap^{\frac{1}{2}}) \frac{m}{T^n}$$

The constants for this equation are

Metric (p in kg. per sq. m.)	English (p in lb. per sq. in.)
$\log B = 1.67274$	$\log B = \bar{1}.77508$
$\log m = 8.65429$	$\log m = 10.88000$
$3a = 0.001131$	$3a = 0.03$
$n = 4$	$n = 4$

In all respects this equation is an improvement over the first equation.

Further consideration of the question led to another slight modification with a corresponding change of constants. Accepting Callendar's suggestion that the first member should contain a term to represent the co-volume, the equation was given the form

$$v - c = \frac{BT}{p} - (1 + 3ap^{\frac{1}{2}}) \frac{m}{T^n} \qquad \text{(B)}$$

and the value of c was taken as the specific volume of water. Hence, when the equation is used to determine the specific volume of saturated steam, the first member becomes simply $v'' - v'$. Since this difference, rather than the steam volume v'', occurs in the Clapeyron relation and

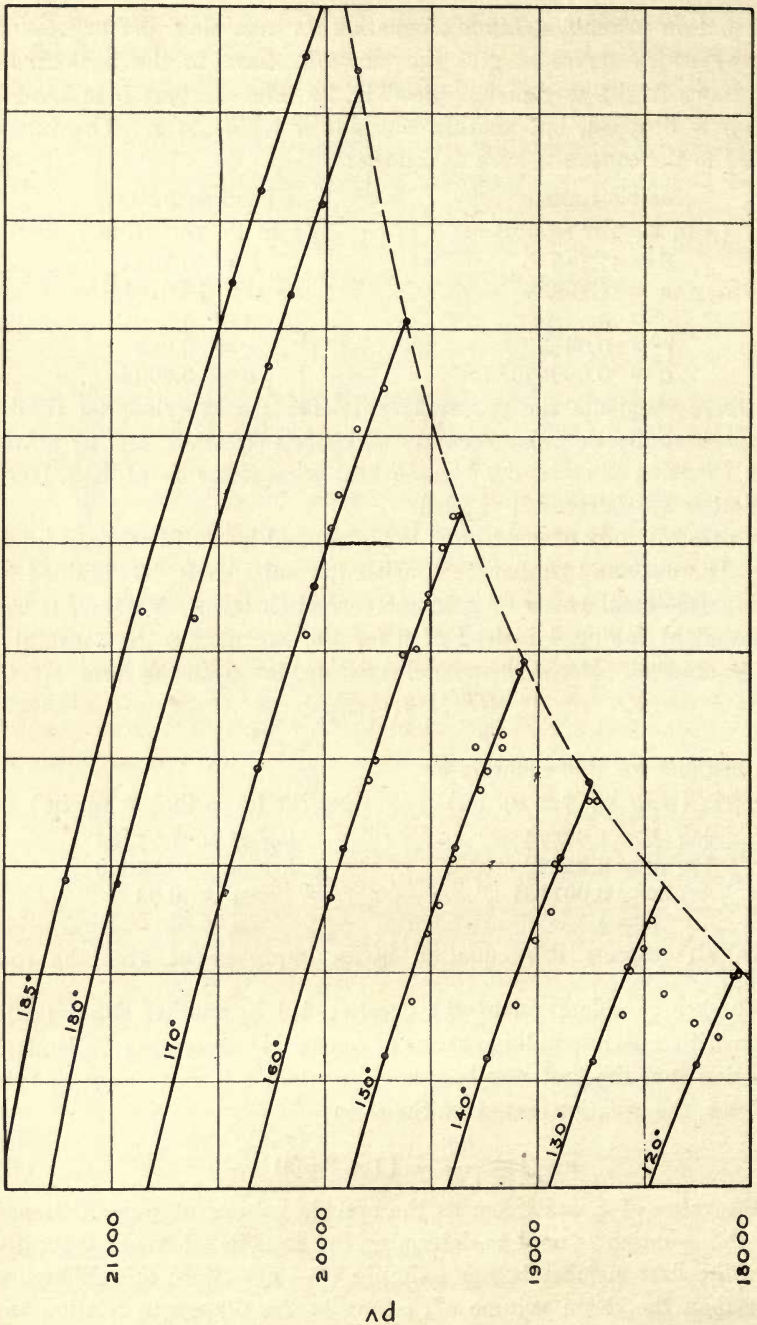

FIG. 2. ISOTHERMAL CURVES FROM EQ. (B). THE POINTS REPRESENT THE EXPERIMENTS OF KNOBLAUCH, LINDE, AND KLEBE.

in other thermodynamic formulas, the inclusion of the constant c really simplifies the calculation of the thermal magnitudes that involve specific volumes. The constants of the final equation are as follows:

Metric	English
$\log B = 1.67206$	$\log B = \bar{1}.77441$
$\log m = 8.59929$	$\log m = 10.82500$
$\log 3a = \bar{3}.28644$	$\log 3a = \bar{2}.71000$
$n = 4$	$n = 4$

With the satisfaction of the Clausius relation in view, Heck[1] has developed an equation which is in form considerably different from any heretofore suggested. It is

$$v = \frac{BT}{p} - \frac{E}{(t+130)^2} - \frac{F}{(t+40)^8}\, p^{1.4}$$

The constants are: $B = 0.5956$, $\log E = 4.66365$, $\log F = 11.02244$. Pressures are to be taken in lb. per sq. *inch*.

It may safely be assumed that Heck's equation represents the volume measurements sufficiently well and that it satisfies the Clausius relation.

20. *Tests of the Characteristic Equation.*—The following comparisons are made to establish the validity of equation (B) as far as specific volumes are concerned. The question of the satisfaction of the Clausius relation is discussed in the following section.

1. Isothermal curves are calculated from (B) and drawn on the pv-p plane along with the points plotted from the measurements of Knoblauch, Linde and Klebe. The result is shown in Fig. 2, which may be compared with Fig. 13 in Linde's paper.[2] The agreement between the curves and points is thoroughly satisfactory.

2. As has been stated, the constant volume lines of Knoblauch, Linde, and Klebe when drawn on the pt-plane appeared to be straight lines. Linde[3] has compared the slopes of these lines as observed with the slopes calculated from his first equation. The slopes *at the saturation limit* have been calculated from (B), and the following table gives a comparison

TABLE 4. VALUES OF $\left(\frac{\partial p}{\partial T}\right)_v$

t =	101.4	112.3	126.5	139.2	150.3	163.2	170	180.6	183
From (B)	30.7	44.0	68.4	99.0	134.7	189.2	224.8	291.5	309.7
Linde	30.4	43.9	67.4	97.9	132.9	188.9	221.7	287.5	303.7
Observed	30.4	44.3	68.0	99.3	134.0	188.6	225.0	293.0	313.0
Heck	30.5			96.3		178.7			285.2

1. Journal Am. Soc. Mech. Eng'nrs, Nov., 1913, p. 1619.
2. Mitteil. über Forschungsarbeit., Vol. 21, p. 58.
3. Loc. cit., p. 67.

The comparison is somewhat misleading, because both Linde's second equation and equation (B) give values of the slope that vary slightly with the temperature. This variation is shown for four of the experiments.

TABLE 5.

VARIATION OF $\left(\frac{\partial p}{\partial T}\right)_v$ WITH TEMPERATURE.

Exper. No. 1	$t = 101.4$	120.0	140.0	160.0
$\left(\frac{\partial p}{\partial T}\right)_v$	$= 30.7$	30.2	30.1	29.9
No. 12	$t = 126.5$	140.0	160.0	180.0
$\left(\frac{\partial p}{\partial T}\right)_v$	$= 68.4$	67.7	67.0	66.9
No. 22	$t = 150.3$	160.0	180.0	
$\left(\frac{\partial p}{\partial T}\right)_v$	$= 134.7$	133.2	131.2	
No. 29	$t = 170.0$	180.0		
$\left(\frac{\partial p}{\partial T}\right)_v$	$= 224.8$	219.9		

The change in slope introduces a curvature in the constant volume lines, so slight however, that it can scarcely be detected in the figure. It is clear that the slopes deduced from (B) agree sufficiently well with the observed slopes.

3. Values of v'', the specific volume of the saturated vapor, as calculated from (B) are compared with values calculated from Linde's equation. The following table shows the comparison:

TABLE 6.

COMPARISON OF SPECIFIC VOLUMES.

Temp. C.	100	110	120	130	140	150	160	170	180
v'' from (B).....	1.6738	1.211	0.8926	0.6692	0.5095	0.3923	0.3075	0.2431	0.1943
v'', Linde.....	1.6740	1.211	0.8922	0.6690	0.5091	0.3921	0.3073	0.2430	0.1943

At the saturation limit the two formulas give practically identical values throughout the range of temperature covered by the experiments.

4. For the range 0°–100° C. and for temperatures above 180° C. there are no reliable experimental values to serve as a check of the formula. However, the specific volumes of the saturated vapor given in the Marks and Davis tables may be accepted as fairly accurate as they

were calculated by means of the Clapeyron relation from values of the latent heat that are at least approximately correct. The following table shows a comparison of volumes obtained from (B) with the Marks and Davis values.

TABLE 7.

COMPARISON OF SPECIFIC VOLUMES.

Temp. F.	32	40	80	120	160	200	212	240	280	320	360	400	440	480	520	560	600
v'' from (B)	3296	2440	632.8	203.2	77.28	33.65	26.81	16.33	8.66	4.92	2.964	1.868	1.220	0.820	0.562	0.391	0.274
v'', M. & D.	3294	2438	632.8	203.1	77.20	33.60	26.79	16.32	8.64	4.91	2.957	1.872	1.229	0.81	0.55	0.39	0.27

From the comparison it appears that formula (B) may be accepted, so far as saturation volumes are concerned, for the entire range 32°–600° F.

5. For the volumes in the region of high superheat there is at present no check. The measurements of Knoblauch, Linde, and Klebe reach only to about 50° C. (120° F.) of superheat. The extension of any formula to 400° or 500° superheat is therefore an extrapolation, the validity of which is uncertain. On account of the character of the correction term in Linde's formula (see p. 26), it is practically certain that at high superheat Linde's values are too high. Jakob[1] in the course of this investigation has deduced values that run consistently lower than those of Linde at the higher superheats. As a matter of interest a comparison has been made between three sets of values for three different pressures, 1, 9 and 19 kg. per sq. cm. This is shown in the following table:

TABLE 8.

SPECIFIC VOLUMES OF SUPERHEATED STEAM.

p = 10000 kg. per sq. m.							
t =	99.1	130	160	190	220	250	300
v from (B)	1.7254	1.8777	2.0233	2.1675	2.3109	2.4536	2.6904
v Linde	1.7260	1.8783	2.0245	2.1695	2.3137	2.4571	2.6954
v Jakob	1.7281	1.8789	2.0237	2.1674	2.3107	2.4535	2.6909
p = 90000							
t =			174.6	190	220	250	300
v from (B)			0.2193	0.2293	0.2480	0.2659	0.2946
v Linde			0.2190	0.2293	0.2483	0.2665	0.2959
v Jakob			0.2195	0.2296	0.2479	0.2655	0.2939
p=190000							
t =				208.9	220	250	300
v from (B)				0.1068	0.1107	0.1208	0.1362
v Linde				0.1068	0.1108	0.1213	0.1374
v Jakob				0.1071	0.1113	0.1210	0.1359

The comparison is shown graphically in Fig. 3. The ordinates of curve L represent the difference between Linde's values and the values given

1. Zeit. des Verein. deutsch. Ing., Vol. 56, p. 1987.

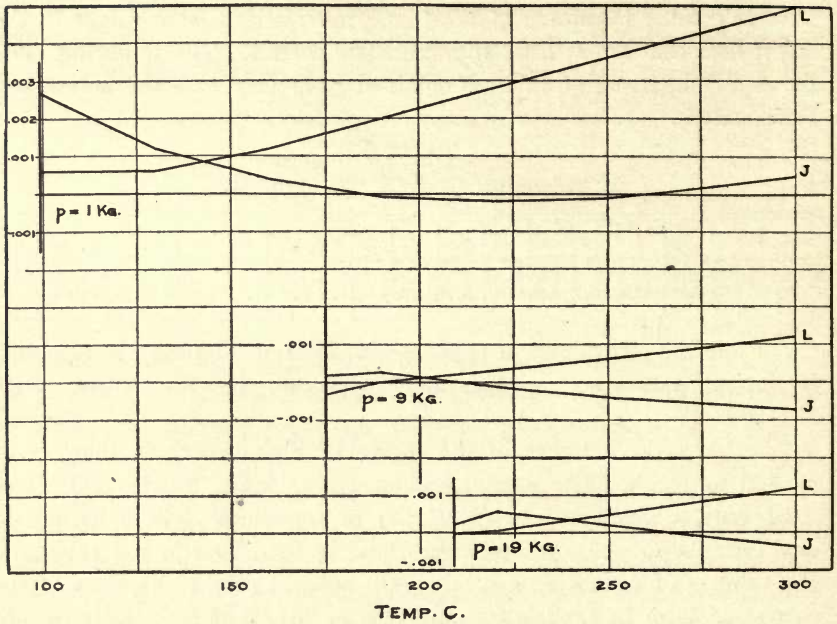

FIG. 3. COMPARISON OF SPECIFIC VOLUMES.

by eq. (B). Similarly, curve J applies to Jakob's values. It will be seen that, in general, the volumes calculated from (B) lie near Linde's volumes at the saturation limit, but approach more nearly Jakob's values with increasing superheat. It will be observed that the curve J cuts the base line (which represents formula (B)) in two points for the pressure of 1 kg. If the superheat is carried sufficiently high at the other pressures, a second intersection will likewise be obtained. The correction term R in Linde's equation changes sign at 402° C., and in Jakob's system the change of sign occurs at 920° C. Hence before reaching 920° Jakob's values must rise above those calculated from (B).

The correction term in eq. (B) does not change sign at any temperature. It approaches zero as T is indefinitely increased, and it becomes negligible compared with the term $\frac{BT}{p}$ when the pressure becomes very small. In these two limiting cases, therefore, equation (B) merges into the equation

$$p\,(v - c) = BT.$$

Evidently the *form* of equation (B) is such as to justify extrapola-

tion beyond the region of the experiments; and it is probable that the values of v calculated from this equation are worthy of confidence both at the saturation limit and in the region of superheat.

C. SPECIFIC HEAT OF SUPERHEATED STEAM.

21. *Experimental Data.*—The experiments on specific heat may be divided into groups as follows:

1. The early experiments of Regnault with steam at atmospheric pressure and at temperatures relatively close to saturation.

2. The experiments of Mallard and Le Chatelier, Langen, and Pier at very high temperatures.

3. The experiments of Holborn and Henning with steam at atmospheric pressure and a temperature range of 110°–1400° C.

4. The experiments of Grindley and Griessmann using the throttling method.

5. Recent direct experiments with steam at various pressures. Of these, the experiments of Knoblauch and Jakob and of Knoblauch and Mollier performed in the Munich laboratory are specially noteworthy. Similar experiments have been made by Thomas.

Regnault's experiments made in 1862[1] indicated a constant value of $c_p = 0.4805$. Davis[2] has recomputed Regnault's values and has deduced a somewhat smaller value, namely, $c_p = 0.4762$. For the pressure and range of temperature covered in the experiment, Regnault's value agrees well with the results of recent experiments.

1. Mem. Inst. de France, Vol. 26, p. 167 (1862).
2. Proc. Am. Acad., Vol. 45, p. 286 (1910).

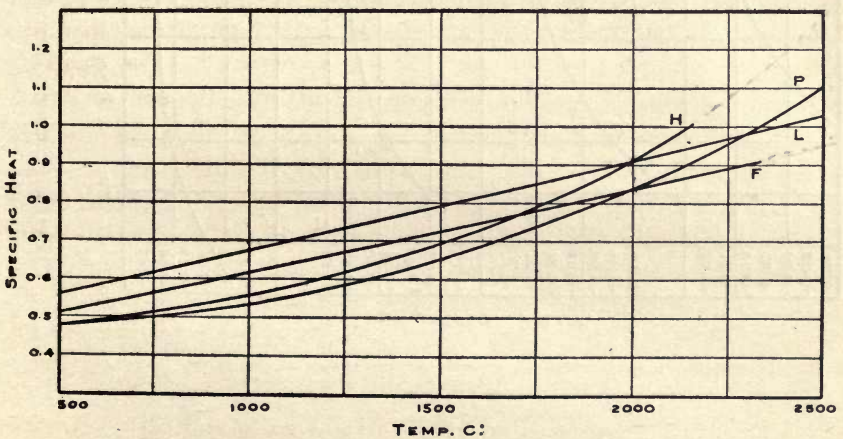

FIG. 4. CURVES OF SPECIFIC HEAT.

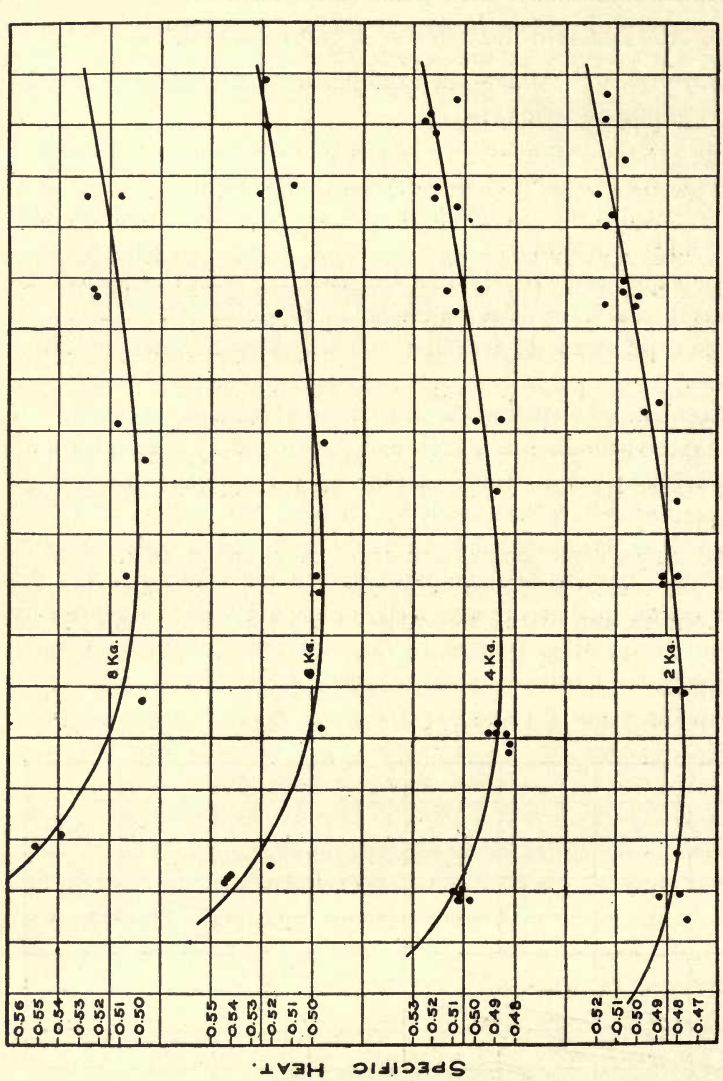

FIG. 5. CURVES OF SPECIFIC HEAT DEDUCED FROM EQ. (C). THE POINTS REPRESENT THE EXPERIMENTS OF KNOBLAUCH AND MOLLIER.

The high temperature experiments noted in group 2 have only an indirect bearing on the present investigation. The results obtained by the different investigators are discordant, but they all agree in showing a marked increase of specific heat with rising temperature. In Fig. 4 the straight line L represents the linear relation

$$c_p = 0.439 + 0.000239t$$

established by Langen, curve P represents Pier's equation, and curve H the equation given by Holborn and Henning.

The experiments of Holborn and Henning[1] form a link between the high temperature experiments of group 2 and the experiments of group 5. These measurements indicate values of c_p consistently lower than those obtained in the Munich experiments. While considerable weight must be attached to the Holborn and Henning experiments, it seems probable that preference must be given the Knoblauch and Mollier measurements. Callendar[2] has expressed the opinion that the Holborn and Henning values are too low by as much as 10 per cent.

The efforts of Grindley and Griessmann to determine c_p by the method of throttling were futile, and the results obtained by them are without value.

Of the direct experiments, preference is justly given to those of Knoblauch and Jakob[3] and Knoblauch and Mollier.[4] The latter experiments supplement and extend the range of the former. A third set of experiments is now being conducted, and preliminary reports indicate that the earlier results will be sustained. The results reported by Thomas[5] are of value indirectly as in some degree corroborating the Munich experiments. As conclusively shown by Davis,[6] the Thomas experiments are not to be compared with the Knoblauch experiments in point of accuracy.

After reviewing all the experimental evidence one must be convinced that for the range of temperature covered, the Knoblauch and Mollier measurements should be accepted without modification. They are therefore used in the present investigation. The points plotted in Fig. 5 are those determined by Knoblauch and Mollier. For convenience in the identification of the measurements associated with the four pressures employed, the points have been separated into four groups.

1. Annalen der Physik, Vol. 18, p. 739 (1905); Vol. 23, p. 809 (1907).
2. Report of British Assoc. Committee on Gaseous Explosions, pp. 31, 32 (1908).
3. Mitteil. über Forschungsarbeit, Vol. 35, p. 109.
4. Zeit. des Ver. deutsch. Ing., Vol. 55, p. 665 (1911).
5. Proc. Am. Soc. Mech. Engrs., Vol. 29, p. 633 (1907).
6. Proc. Am. Acad. of Arts and Sciences, Vol. 45, pp. 269-272.

22. *Systems of Specific Heat Curves.*—The Knoblauch and Jakob experiments showed unmistakably the variation of specific heat with both pressure and temperature. At constant temperature, an increase of pressure resulted in an increase of specific heat; and at constant pressure the value of c_p first decreased from the saturation limit, attained a minimum and then increased. Knoblauch and Jakob exhibited the variation of c_p by means of constant pressure curves drawn on a plane with c_p as ordinate and t as abscissa. The curves were so drawn as to represent as closely as possible the experimental points and by a doubtful process of extrapolation the pressures were carried up to 20 kg. per sq. cm.

Taking the Knoblauch and Jakob curves as a basis, Davis developed a system of specific heat curves (Marks and Davis, Steam Tables and Diagrams, p. 97) from which the properties of superheated steam were deduced. Davis modified the Knoblauch curves in two respects. 1. Accepting the Holborn and Henning measurements, he lowered the c_p curve for atmospheric pressure so that it would join the Holborn and Henning curve. In the light of the Knoblauch and Mollier results, this modification was doubtless a mistake. 2. The Knoblauch values at low pressures near the saturation limit were changed so as to bring them more nearly in accord with Regnault's value. Davis also developed a thermodynamic relation by which the spacing of the curves could be tested. Denoting by μ the Joule-Thomson coefficient, the relation is

$$\frac{c_p}{c_{po}} = e^{-\int_{p_o}^{p} \left(\frac{\partial \mu}{\partial T}\right)_p dp} \tag{12}$$

Davis had already investigated the Joule-Thomson effect for steam[1] and had obtained an approximate relation between μ and t. By means of the relations $\mu = f(t)$ he was able to evaluate the integral in (12) and thus to adjust the spacing of the c_p-curves.

Another system of c_p-curves has been worked out by Jakob.[2] The curves were adjusted to the Knoblauch and Mollier points, from Davis' relation the curve for c_{po} (*i. e.*, p = 0) was determined, and then by the same relation c_p-curves for 10, 12, 14, 16, 18, and 20 kg. per sq. cm. were established. Near the saturation limit the Jakob curves agree closely with the Davis curves; at the higher superheats the increase of c_p with the temperature is more marked in the Jakob curves, as it doubtless should be.

1 Proc. Amer. Acad. of Arts and Sciences, Vol. 45, p. 261.
2. Zeit. des Verein. deutsch. Ing., Vol. 56, pp. 1981-3 (1912).

23. *Equation for Specific Heat.*—From the characteristic equation

$$v - c = \frac{BT}{p} - (1 + 3ap^{\frac{1}{2}}) \frac{m}{T^n}$$

the second derivative required in the Clausius relation is obtained. It is

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = -(1 + 3ap^{\frac{1}{2}}) \frac{mn(n+1)}{T^{n+2}}.$$

Hence

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -AT \frac{\partial^2 v}{\partial T^2} = \frac{Amn(n+1)}{T^{n+1}} (1 + 3ap^{\frac{1}{2}}).$$

An integration with T constant gives an expression for c_p, namely

$$c_p = F(T) + \frac{Amn(n+1)}{T^{n+1}} p(1 + 2ap^{\frac{1}{2}}).$$

The arbitrary function $F(T)$ is evidently c_{po}, that is, the specific heat at zero pressure. This was taken as a constant by Callendar. The experiments of Knoblauch and Mollier show that c_{po} cannot be constant, and this conclusion is confirmed by the high-temperature experiments of Langen and others. It has been suggested that a simple linear relation

$$c_{po} = \alpha + \beta T$$

may be assumed, and this assumption was made in the writer's earlier paper. It is found, however, that better agreement is obtained by a relation of the form

$$c_{po} = \alpha + \beta T + \frac{\gamma}{T^2}.$$

Writing the equation for c_p in the form

$$c_p = F(T) + f(p, T)$$

values of the term $f(p, T)$ may be calculated for each of the Knoblauch and Mollier experiments and by subtraction the corresponding values of $c_{po} = F(T)$ are found. From the curve through these points the constants α, β, and γ are obtained. The equation for c_p finally takes the form

$$c_p = \alpha + \beta T + \frac{\gamma}{T^2} + \frac{Amn(n+1)}{T^{n+1}} p(1 + 2ap^{\frac{1}{2}}) \qquad (C)$$

and the constants are

	Metric	English
α	0.320	0.320
β	0.0002268	0.000126
γ	7371	23583

The constants a, m, and n are those of the characteristic equation. (See p. 29.)

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In Fig. 5 the curves calculated from equation (C) are shown. The agreement between the curves and experimental points is sufficiently evident. It would be difficult to obtain a family of curves connected by a relation that would represent more accurately the groups of points.

The perfect correlation of the Munich experiments is shown by a comparison of Figs. 2 and 5. Equation (B) gives the curves of Fig. 2, equation (C) the curves of Fig. 5. The equations certainly represent the experimental data within the limits of accuracy of the experiments, and they are properly connected by the Clausius relation. The difficulty of making the correlation lies not in the measurements themselves,—they are sufficiently accurate—but in the choice of a proper form for the characteristic equation. The results here shown amply justify the method used in attacking the problem, and they strongly confirm the validity of equation (B).

In the following table values for c_p for various temperatures and pressures are given. The numbers in parentheses are the corresponding values deduced by Jakob from his c_p-curves:

TABLE 9.

SPECIFIC HEAT OF SUPERHEATED STEAM.

Pressure kg. per sq. cm.	Temperature C								
	150	200	250	300	350	400	450	500	550
0	0.457	0.460	0.466	0.473	0.480	0.489	0.498	0.508	0.518
	(0.462)	(0.465)	(0.469)	(0.474)	(0.481)	(0.489)	(0.497)	(0.505)	(0.514)
2	0.490	0.479	0.477	0.480	0.485	0.492	0.500	0.509	0.519
	(0.486)	(0.477)	(0.477)	(0.480)	(0.485)	(0.492)	(0.500)	(0.508)	(0.516)
4	0.527	0.498	0.489	0.487	0.490	0.496	0.503	0.511	0.520
	(0.524)	(0.494)	(0.486)	(0.486)	(0.490)	(0.496)	(0.503)	(0.510)	(0.517)
6		0.522	0.503	0.496	0.496	0.500	0.505	0.513	0.521
		(0.514)	(0.495)	(0.492)	(0.494)	(0.500)	(0.506)	(0.512)	(0.518)
8		0.545	0.517	0.504	0.502	0.504	0.508	0.515	0.523
		(0.538)	(0.505)	(0.498)	(0.499)	(0.503)	(0.508)	(0.514)	(0.520)

The agreement between the two sets of values is remarkably close; except for three or four points the difference is well within one per cent. From 350° to 500° the values are practically identical, but above 500° the specific heats calculated from the equation begin to rise above the values found by Jakob, while these in turn are higher than the Davis values. The question of the proper course of the c_p-curves at 550° is important in connection with the c_p values at high superheat. The only guide in settling this question is the experimental evidence furnished by the high-temperature experiments. Referring to Fig. 4, curve F represents the function $F(T) = \alpha + \beta T + \frac{\gamma}{T^2}$ and at high tempera-

tures this curve is practically identical with the specific heat curve, since the term $f(p, T)$ in the specific heat equation becomes vanishingly small. It will be seen that curve F is in good agreement with the other curves between 500° and 2000° C. If Jakob's curves were prolonged in the same way, they would merge into a single curve lying somewhat below curve F. This is more clearly shown in Fig. 6, in which various determinations of the function $c_{po} = F(T)$ are plotted. Curve H represents the variation of c_{po} assumed by Heck, curve A represents the preceding equation, and the points are plotted from the values of c_{po} given

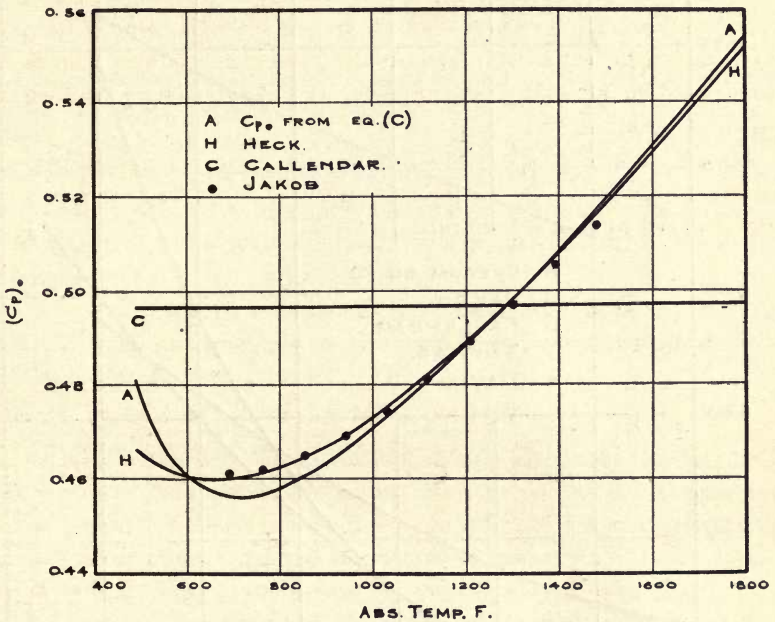

FIG. 6. CURVES OF SPECIFIC HEAT $(C_p)_o$.

by Jakob. As a matter of interest Callendar's constant value is shown by the straight line C. It appears that the three curves agree quite well. At the higher temperatures curves A and H are almost coincident, but the Jakob points show a tendency to run low. It is probable that equation (C) gives fairly good values of c_p up to about 2000° C., that Heck's equation may safely be used through the same range, but that Jakob's curves if prolonged lie somewhat low and are not valid above 1000° C.

At the lower temperatures Heck and Jakob are in close agreement, while curve A shows quite a different course. Experimental evidence in

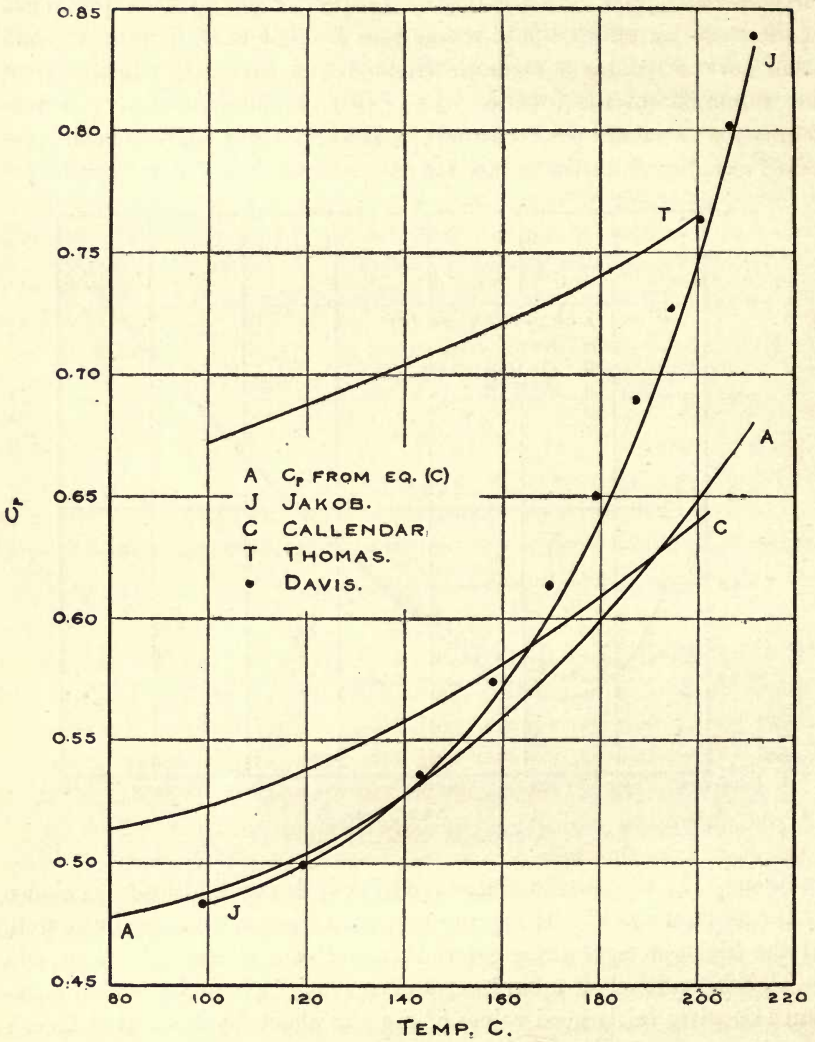

FIG. 7. CURVES OF SPECIFIC HEAT AT THE SATURATION LIMIT.

this region is entirely lacking, and consequently no statement can be made as to the probable relative accuracy of the two curves.

In all discussions of specific heat much emphasis has been laid on the values of c_p at the saturation limit. These give a "saturation curve." From the specific heat equation (C) values of $(c_p)_{sat}$ are readily calculated by taking for p and t corresponding saturation values. Curve *A*, Fig. 7, is the curve thus derived. Davis[1] has given a very full discussion of this subject. The empirical curves of Knoblauch and Jakob were tested by Planck's thermodynamic relation

$$(c_p)_{sat} = \frac{dH}{dt} - \frac{r}{T} + AT\left(\frac{\partial v}{\partial t}\right)\left(\frac{dp}{dt}\right)_{sat}$$

and fair agreement was shown. Davis therefore accepted the Knoblauch values of $(c_p)_{sat}$ with a reservation. Regarding the tremendous rise of Knoblauch's saturation curve at even moderately high temperatures he says: "It is probable that this feature of Knoblauch's curves, although near enough the truth to satisfy the present needs of engineering practice, will have to be revised later." The points in Fig. 7 represent the values of $(c_p)_{sat}$ given by Davis.

Jakob arbitrarily established the values of $(c_p)_{sat}$ for four pressures: 2, 4, 6, and 8 kg. per sq. cm., and from these determined the constants in the assumed formula.

$$(c_p)_{sat} = 0.455 + 2 \cdot 10^{-20} \frac{T_s^8}{T_k - T_s}$$

in which T_s denotes the saturation temperature and T_k the critical temperature. The curve thus found is curve *J*, Fig. 7. It agrees very closely with the Davis curve but runs slightly lower. According to Jakob's formula $(c_p)_{sat}$ becomes infinite at the critical temperature.

Curve *T*, Fig. 7, represents the experiments of Thomas, and curve *C*, the saturation values of c_p calculated by Callendar from purely theoretical considerations.

It is a safe conclusion that curve *A* is nearer the truth than curve *J* or the Davis curve. In the first place, the values represented by curve *A* are obtained from an equation, and as shown in Fig. 5, this equation represents very accurately the best experimental data. The equation automatically extends the curves from the region of the experiments to the saturation curve, thus obviating a doubtful extrapolation that was necessary in laying down the empirical curves. Again, the relation of the curves to the experimental points exhibited in Fig. 5 indicates accurate spacing. The curves show no tendency to run high or low

1. Proc. Am. Acad., Vol. 45, pp. 295-303.

with increasing pressure. Hence it appears probable that equation (C) may be used with confidence for pressures considerably higher than those used in the experiments. At any rate, there is no reasonable doubt that the c_p-curve for a pressure of 20 at. calculated from eq. (C) is likely to be nearer the truth than the corresponding curve obtained by the system of extrapolation employed by Knoblauch and Jakob.

It should be observed that the Davis equation for spacing the curves (see p. 36) and Planck's thermodynamic relation are both automatically satisfied, as both reduce to identities when applied to the equations developed in this investigation.

While Regnault's measurements of c_p at atmospheric pressure are not to be considered as possessing any great degree of precision, some importance may be attached to a comparison of Regnault's results with the corresponding values of c_p calculated from equation (C). The four series of experiments covered the temperature range 122.8°–231.1° C. The mean value of c_p given by Regnault was 0.4805, but this value is lowered to 0.4762 by Davis. All experiments were conducted at atmospheric pressure. The following table gives values of c_p at atmospheric pressure calculated from the equation, also the values assigned by Jakob for the slightly lower pressure, 1 kg. per sq. cm.

TABLE 10.

SPECIFIC HEAT AT ATMOSPHERIC PRESSURE.

Temp. C.	100	150	200	250	300	350	400
From Eq. (C).....	0.489	0.474	0.470	0.472	0.476	0.483	0.491
Jakob.....	0.482	0.473	0.471	0.473	0.477	0.483	0.490

The mean c_p deduced from the equation agrees very well with the recomputed value 0.4762, and the Regnault experiments therefore strengthen the evidence in favor of the specific heat equations.

D. TOTAL HEAT, LATENT HEAT, HEAT OF LIQUID.

24. *Equation for Heat Content.*—From the characteristic equation and the equation for specific heat an expression for the heat content is readily deduced. In the general equation

$$di = c_p\,dT - A\left[T\left(\frac{\delta v}{\delta T}\right)_p - v\right]dp$$

we introduce the expression for c_p given by eq. (C) and the expression for the derivative $\left(\frac{\delta v}{\delta T}\right)_p$ obtained from the characteristic equation, namely

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{B}{p} + \frac{mn}{T^{n+1}}(1 + 3ap^{\frac{1}{2}}).$$

The result of the substitutions is the equation

$$di = \left[a + \beta T + \frac{\gamma}{T^2} + \frac{Amn\,(n+1)}{T^{n+1}} p\,(1 + 2ap^{\frac{1}{2}})\right] dT$$

$$- A\left[\frac{m\,(n+1)}{T^n}(1 + 3ap^{\frac{1}{2}}) - c\right] dp,$$

which upon integration gives the following equation for the heat content

$$i = aT + \tfrac{1}{2}\beta T^2 - \frac{\gamma}{T} - \frac{Am\,(n+1)}{T^n} p\,(1 + 2ap^{\frac{1}{2}}) + Acp + i_o. \quad \text{(D)}$$

The constant i_o is determined as follows. Corresponding saturation values of p and t at some definite temperature, say 212°, are substituted in the equation, which for this purpose may be written

$$i_{sat} = \phi\,(p, T) + i_o.$$

The function $\phi\,(p, T)$ is thus calculated, and i_{sat} being known, i_o is found by subtraction.

Since the constant c is taken as the liquid volume v', the term Acp is Apv', which (see p. 6) is the small difference between the heat content i'' and the total heat q''. Hence, when applied at the saturation limit, equation (D) gives i'' and the same equation with the term Acp omitted gives q''.

25. *Tests of the i-equation.*—Three tests may be applied to the equation (D) for heat content. Two of these apply at the saturation limit, the third in the region of superheat.

1. Values of i_{sat} calculated from equation (D) are compared with values obtained independently by other means. The following table shows a comparison with the Marks and Davis values for i:

TABLE 11.

HEAT CONTENT OF SATURATED STEAM.

Temp. F.	i''		Temp. F.	i''		Temp. F.	i''	
	Eq. (D)	M. & D.		Eq. (D)	M. & D.		Eq. (D)	M. & D.
32	1072.83	1073.4	212	1151.58	1150.4	440	1202.33	1207.1
40	1076.64	1076.9	240	1161.90	1160.4	480	1200.43	1210
80	1095.30	1094.8	280	1175.15	1173.3	520	1194.02	1207
120	1113.34	1112.3	320	1186.30	1184.4	560	1182.76	1196
160	1130.64	1129.5	360	1194.86	1193.7	600	1166.	1176
200	1146.94	1145.8	400	1200.37	1201.3			

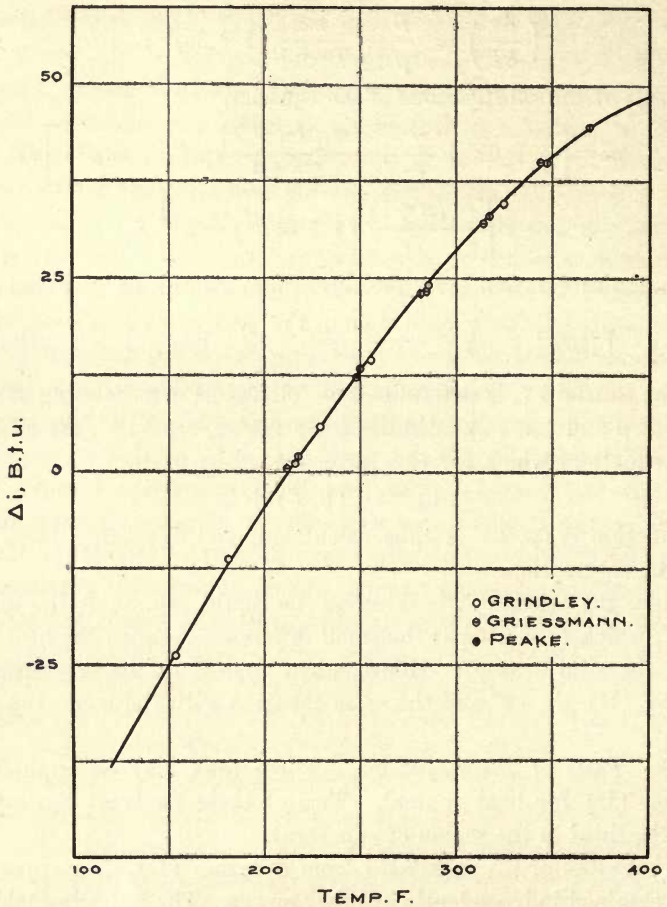

FIG. 8. COMPARISON OF i″-CURVE FROM EQ. (D) WITH POINTS DEDUCED FROM THE THROTTLING EXPERIMENTS.

The considerable discrepancy above 400° has no significance, for in this range Davis makes no claim for the accuracy of the M. and D. values. The effective test is furnished by a comparison of the two sets of values within the range 212° — 400°, where the Davis formula for heat content is surely valid. The comparison is shown graphically in Fig. 8. The points are those determined by Davis from the throttling experiments of Grindley, Greissmann and Peake, and they are plotted from the data given in Table 1 of Davis' paper.[1] The ordinates represent

1. Proc. Am. Acad., Vol. 45, p. 276.

the difference between the i at the given temperature t and the i at 212°. The curve therefore represents the equation

$$i'' - i''_{212} = f(t),$$

where i'' is calculated from the formula and $i''_{212} = 1151.58$. The curve does not fit the points quite as well as the Davis second-degree curve, but the agreement is satisfactory, and is probably well within the limits of accuracy of the throttling experiments. Beyond the last point the curve begins to bend downward rather sharply and thus diverge from the prolonged Davis curve. The maximum value of i'' is reached at about 440°, the Davis equation gives the maximum at about 550°, and in the Marks and Davis tables the maximum occurs at 480°.

2. The Clapeyron-Clausius relation furnishes a valuable test within the range 32° — 212° (see p. 7). The discussion of this point is given in another section.

3. In the region of superheat the heat content formula may be checked by the throttling experiments of Grindley, Griessmann and Peake. According to the principles of thermodynamics a throttling process is also a constant-i process. That is, the points obtained in any particular throttling experiment when plotted on the p, t plane should lie on a curve $i = \text{const.}$

In Fig. 9 the points are plotted from the experiments of Peake and Grindley, and constant-i curves calculated from eq. (D) are superposed. The general agreement is satisfactory, especially at the lower pressures. At the highest pressures Peake's highest curve has a smaller slope than the curve for $i = 1200$ and intersects it. It will be observed, however, that the curve has the slope indicated by Peake's points near saturation and the slope indicated by Grindley's points at some distance from the saturation limit.

The divergence of the curves from Peake's points naturally suggests the possibility that the curves run too low at the higher superheats. If this were the case, values of i calculated from equation (D) would be somewhat greater than the true values. Some light is thrown on this point by the series of throttling experiments made by Dodge.[1] In these experiments the steam was initially highly superheated, and the initial pressure was about 300 lbs. per sq. in. gauge. The points of 14 tests are shown in Fig. 10; these were taken directly from Davis'[2] discussion of the throttling experiments. Through each group of high-side points

1. Jour. A. S. M. E., Vol. 28, p. 1265 (1907); Vol. 30, p. 1227 (1908).
2. Proc. Am. Acad., Vol. 45, p. 253-257.

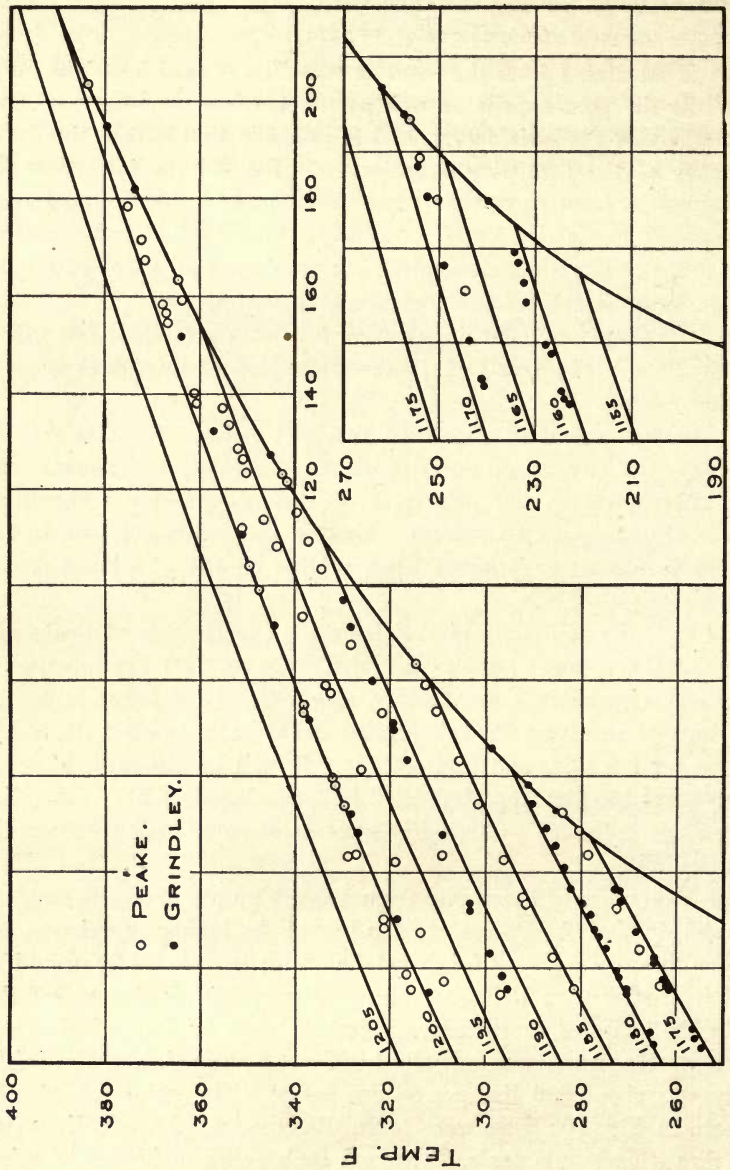

FIG. 9. CURVES OF CONSTANT HEAT CONTENT.

a constant-*i* curve has been drawn. It will be seen that the curves agree fairly well with the points and at the higher superheats have the slopes indicated by general trend of the points. The marked drop from the initial point to the first of the low-side points is a phenomenon that is difficult to explain. In this connection Davis says: "It will be noticed that in every case a smooth curve through the low side points runs considerably below the corresponding high side points, just as did Grindley's

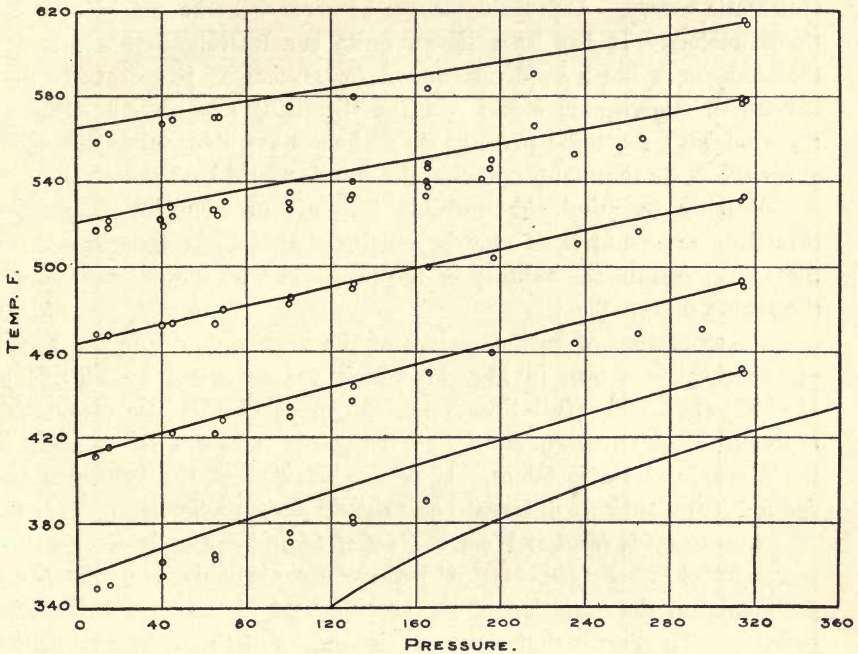

FIG. 10. COMPARISON OF CONSTANT-i CURVES WITH POINTS FROM DODGE'S THROTTLING EXPERIMENTS.

curves. In Grindley's case this was because the entering steam carried water in suspension, the presence of which made the true total heat of the incoming mixture less than its apparent total heat regarded as homogeneous saturated steam, and dropped all the low side points onto throttling curves lower than those on which they apparently belonged. A similar phenomenon may be in evidence in Dodge's case, for although the incoming steam was superheated, it may still have been carrying in suspension a part of the water which had been sprayed into it for temperature regulation just before it reached the high-side chamber. It must, however, be admitted that if this explanation is to account for the whole of the discrepancy in Dodge's results, an extraordinarily large

amount of water in suspension must have reached the high-side chamber —from one to one and a half per cent of the whole weight present. It is therefore probable that there is another source of error not yet discovered."

At the high superheats employed by Dodge it appears unlikely that such an amount of water could have been present, and it is probable that all the throttling experiments were vitiated to some extent by systematic errors. A probable source of error was the use of mercury thermometers. It has been shown quite conclusively that a mercury thermometer is not a good instrument for measuring temperatures in a current of superheated steam. If the throttling experiments could be repeated with the same precautions as have been observed in the other experiments on thermal properties, the results would have great value.

Bearing in mind the probable lack of precision in the sets of throttling experiments, it may be concluded that these experiments, on the whole, sustain the validity of the proposed heat content equation in the region of superheat.

A comparison of various values of the heat content i in the region of superheat is shown in Fig. 11, which was suggested by Fig. 21 of Heck's paper. The full lines represent equation (D), the dash lines represent Heck's new equation, and the points represent values given in the Marks and Davis tables. It is significant that the two equations deduced from entirely different bases should agree so closely.

26. *Specific Heat of Water. Heat of Liquid.*—For the temperature range 32°–212° F. (0°–100° C.) there are available five sets of experiments on the variation of the specific heat of water with the temperature. The curves that represent the results of these experiments are separable into two groups having quite different characteristics. Ludin[1] working with the method of mixtures obtained a curve which shows a minimum value of c' at about 20° C., then a rapid rise to a maximum at 87° C. (See Marks and Davis Steam Tables, Fig. 1, p. 88). The curves obtained by Dieterici[2] and Barnes[3] are similar in character; each shows a decrease of c' to a well defined minimum then a steady rise without any suggestion of a maximum. The experiments of Regnault and Dieterici above 100° C. show a steady rise of the specific heat with the temperature; hence if Ludin's curve be accepted, the specific heat after reaching its maximum at 87° must diminish and then increase

1. Inaug. Diss. Zurich, 1895.
2. Annalen der Physik (4), Vol. 16, pp. 593-620 (1905).
3. Phil. Trans., Vol. 199-A, pp. 55-148, 149-263 (1902).

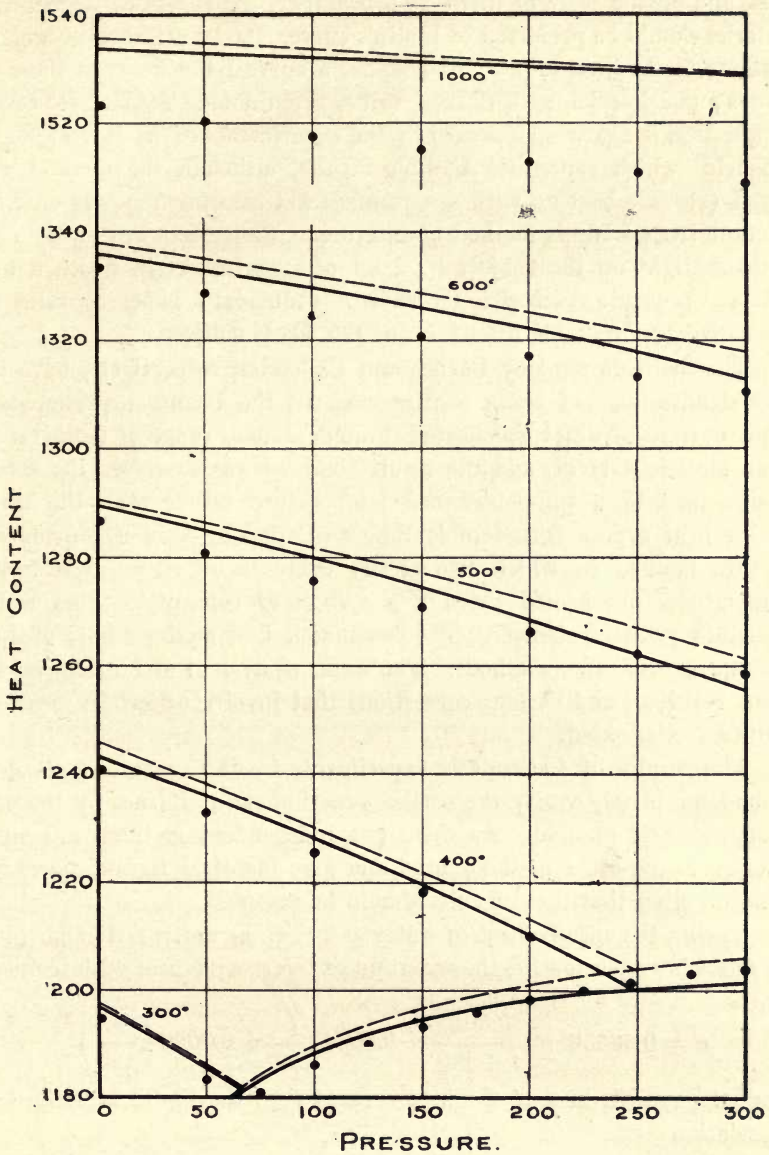

FIG. 11. ISOTHERMAL CURVES ON THE IP-PLANE.

again. It is difficult to account for such a variation on any rational basis, and on the score of intrinsic probability, the curves of Barnes and Dieterici should be preferred to Ludin's curve. Davis[1] attached no weight whatever to Ludin's values and adopted a curve lying between those of Barnes and Dieterici, with Barnes' values given double weight. However, the question is again complicated by the experiments of W. R. and W. E. Bousfield[2] which reproduce Ludin's results, although the method employed (electric heating with a vacuum-jacket calorimeter) was entirely different from Ludin's method of mixtures. Callendar[3] has undertaken to throw light on the subject by a set of experiments in which a new and very accurate method is employed. Callendar's paper contains an exhaustive and valuable discussion of the whole subject.

The methods used by Barnes and Callendar, respectively, have the marked advantage of being continuous. In the Barnes experiments a steady current of water was heated through a small range of temperature by an electric current, and the result obtained was therefore the actual specific heat at a pre-determined temperature rather than the mean specific heat over a considerable range. Callendar used a continuous-mixture method in which two steady currents of water at different temperatures are passed through a system of concentric tubes which constitute a heat exchanger. The continuous flow methods have obvious advantages over other methods. The water equivalent of the calorimeter is not required, and various corrections that involve uncertain measurements are eliminated.

The results of Callendar's experiments by the continuous-mixture method completely verify the earlier experiments of Barnes by the continuous-electric method. As these two independent methods are much superior to the other methods used and give identical results, there can be no question that these results should be accepted.

Taking the specific heat of water at 20° C. as unity, Callendar gives the following equation for the variation of the specific heat with temperature

$$c' = 0.98536 + \frac{0.504}{t + 20} + 0.0084\frac{t}{100} + 0.0090\left(\frac{t}{100}\right)^2.$$

From the specific heat c' the heat content i' of the liquid is derived by the relation

$$i' = \int c'dt.$$

1. Steam Tables and Diagrams, p. 89.
2. Phil. Trans., Vol. 211-A, pp. 199-251 (1911).
3. Phil. Trans., Vol. 212-A, pp. 1-32 (1913).

After changing from C. to F. temperatures and applying a factor to reduce from the 20°-calorie to the mean calorie, the equation for i' becomes

$$i' = 0.9838t + 2.0856 \log (t+4) + 0.233 \left(\frac{t-32}{100}\right)^2 + 0.09245\left(\frac{t-32}{100}\right)^3 - 34.73.$$

Between 32° and 212° this equation gives values that agree very closely with the Marks and Davis values, as shown by the following table.

TABLE 12.

HEAT CONTENT OF LIQUID, 32°–212° F.

Temp. F.	40	80	120	160	200	212	240
Callendar	8.05	48.05	87.94	127.87	167.94	180	208.2
M. & D.	8.05	48.03	87.91	127.86	167.94	180	208.3

For temperatures above 212°, two sets of experiments are available, Regnault's and Dieterici's, neither of which can be accepted as thoroughly reliable. Regnault's results have been recomputed by various investigators. In Fig. 12, six mean values deduced from Callendar's computation are shown. The ordinates in this figure represent values of

$$\Delta i' = i' - (t - 32),$$

that is, the excess of the heat content over $t - 32$, the temperature range.

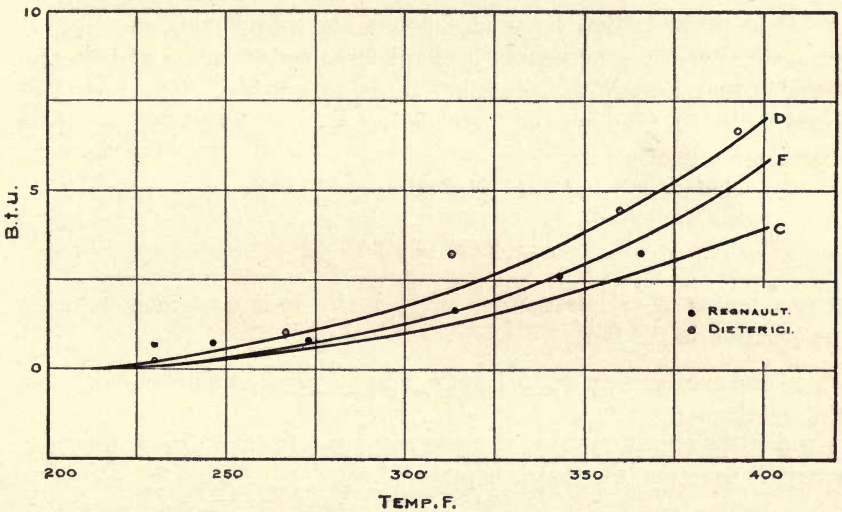

FIG. 12. HEAT CONTENT OF WATER, 212°-400° F.

Abscissas are temperatures F. In the same figure are shown five points obtained by Dieterici, and in Fig. 13, the temperature range is extended and all of Dieterici's points are plotted. The curve *D*, Fig. 12, represents the equation adopted by Dieterici and curve *C* represents Callendar's equation extended beyond 212°.

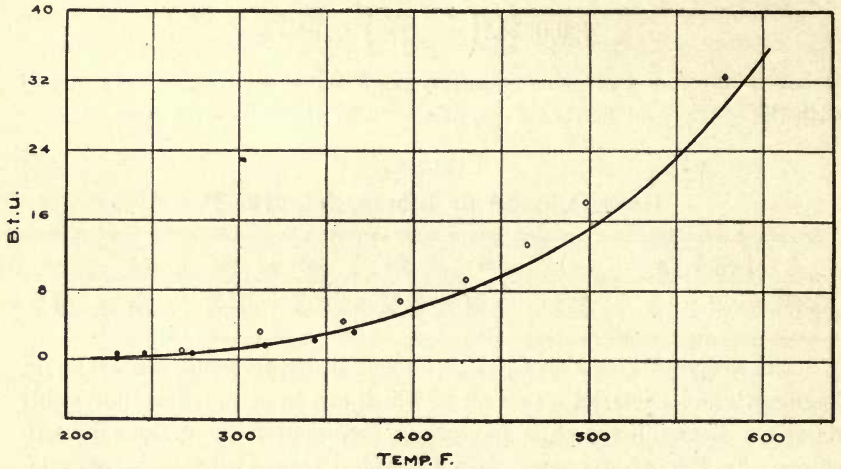

FIG. 13. HEAT CONTENT OF WATER, 212°-600° F.

Callendar questions the accuracy of Dieterici's experiments and gives preference to his equation extrapolated through the range 100° — 200° C. It is probable that Dieterici's points are considerably in error, as the method of the experiments involved large corrections, and it is also probable that Regnault's points are no more reliable. However, there seems to be no valid reason for choosing a curve, like curve *C*, lying below both sets of points.

27. *Latent Heat of Saturated Steam.*—The Clapeyron relation

$$r = A\ (v'' - v')\ T\ \frac{dp}{dT}$$

gives a means of calculating the latent heat. It is convenient to write the equation in the form

$$r = Ap\ (v'' - v')\ \frac{T}{p}\ \frac{dp}{dT}$$

in which the second member is made up of two factors. From the characteristic equation, the first is expressed by

$$Ap\ (v'' - v') = ABT - Ap\ (1 + 3ap^{\frac{1}{2}})\ \frac{m}{T^n}\ .$$

Upon differentiating equation (A) connecting the pressure and temperature of saturated steam, namely

$$\log p = A - \frac{B}{T} - C \log T - DT + ET^2 - \Delta$$

the second factor is obtained in the form

$$\frac{T\,dp}{p\,dT} = 2.3026 \left[\frac{B}{T} - DT + 2ET^2 - T\,\frac{d\Delta}{dt} \right] - C$$

For the range 32° — 212°, within which the heat of the liquid is given accurately by the experiments of Barnes and Callendar, a second independent method of calculating the latent heat is available. Saturation values of i are calculated from the formula for heat content and from these are subtracted the corresponding known values of the heat of the liquid. The difference gives, of course, the latent heat. The following table gives values of r obtained by the two methods, and for comparison the Marks and Davis values are included.

TABLE 13.

LATENT HEAT, 32°–212° F.

Temp. F.	32	40	80	120	160	200	212
i'' from Eq. (D)	1072.83	1076.64	1095.30	1113.34	1130.64	1146.94	1151.58
i' Barnes & Callendar	0	8.05	48.05	87.94	127.87	167.94	180.00
r by subtraction	1072.83	1068.59	1047.25	1025.40	1002.77	979.00	971.58
r by Clapeyron relation	1072.19	1067.96	1046.81	1025.11	1002.62	978.97	971.58
r Marks & Davis	1073.4	1068.9	1046.7	1024.4	1001.6	977.8	970.4

Above 212° the heat of the liquid is so uncertain that the method of determining r by subtraction is hardly justified. Hence values of r are calculated from the Clapeyron relation, and subtracted from corresponding values of i''. The result is a set of values of i' that may be compared with the Regnault and Dieterici experimental values. The following table exhibits the details of the calculation.

TABLE 14.

LATENT HEAT AND HEAT OF LIQUID, 212°–600° F.

Temp. F.	212	240	280	320	360	400	440	480	520	560	600
i'' from Eq. (D)	1151.58	1161.90	1175.15	1186.30	1194.86	1200.37	1202.33	1200.43	1194.02	1182.76	1166.00
r from Clap. rel.	971.58	953.73	926.42	896.51	863.45	826.66	785.60	739.64	687.96	629.55	563.06
i' by subtraction	180	208.17	248.73	289.79	331.41	373.71	416.73	460.79	506.06	553.21	602.93
r Marks & Davis	970.4	952.1	924.3	894.2	861.8	827.2	790.1	748	700	642	572
i' " " "	180	208.3	249.0	290.2	331.9	374.1	417	462	507	554	604

Referring to the first of the preceding tables, the close agreement of the two sets of values of r may be noted. The greatest difference, which occurs at 32°–40° is about 6 in 10 000. This agreement is a decisive test of the validity of the analysis. The two sets of numbers are obtained independently, one from the characteristic equation, the other from the heat-content equation, and the agreement between the two shows the satisfaction of the Clapeyron relation. Of the two sets the one obtained from the heat-content equation should be chosen, rather than the set derived by means of the Clapeyron relation. The reason for this lies in the slight uncertainty in the exact value of the derivative $\frac{dp}{dt}$ at low temperatures. It was shown in connection with Fig. 1 that the course of the Scheel and Heuse points indicates that the true value of this derivative at 32° is probably slightly greater than the value obtained from either of the three formulas. The slightly lower values of r calculated from the Clapeyron relation in the range of 32° — 80° may be ascribed, therefore, to a small error in the derivative.

For the range 212°–600° the important result is the set of values of i', heat of the liquid. The fairly close agreement of these values with the Marks and Davis values will be observed. The latter numbers were calculated from the Dieterici formula. In Fig. 12 curve F represents the new set of values for the range 212°–400° F., and in Fig. 13 the curve is extended to 600° F. The curve lies between Dieterici's curve and Callendar's extrapolated curve and represents very well the Regnault experiments as interpreted by Callendar. Above 400° the curve runs from 1 to 3 B. t. u. lower than the Dieterici points, a deviation of 0.2 to 0.6 per cent. Dieterici admits a possible error of 0.3 to 0.5 per cent in the experiments to determine the mean specific heat c_m and a further error in the reduction of c_m to the actual specific heat. It is likely that a possible error of at least 1 per cent may be attached to Dieterici's points; hence if the points are too high, as is indicated by Regnault's experiments and Callendar's extrapolated formula, the curve probably represents the true values fairly well.

28. *Experiments on Latent Heat.*—The values of the latent heat r given in Table 13 may be compared with direct experiments within the range 32°–212°. For this purpose four sets of experiments are available, those of Dieterici,[1] Griffiths,[2] Smith,[3] and Henning.[4] The

1. Annalen der Physik, Vol. 37, pp. 494-508 (1889).
2. Phil. Trans., Vol 186-A, pp. 261-341 (1895).
3. Phys. Review, Vol. 25, pp. 145-170 (1907).
4. Annalen der Physik (4), Vol. 21, pp. 849-878 (1906).

following table gives the results of these experiments expressed in a common unit, the mean B. t. u.

TABLE 15.

EXPERIMENTAL DETERMINATIONS OF LATENT HEAT.

	Temp. F.	Latent Heat B. t. u.
Dieterici	32	1072.9
Griffiths	86	1045.1
	104.3	1034.1
Smith	57.1	1061.6
	70.1	1054.5
	82.5	1047.6
	103.6	1035.0
Henning	86.2	1043.2
	120.5	1026.2
	148.7	1008.0
	171.2	995.4
	192.7	983.3
	213.1	969.8

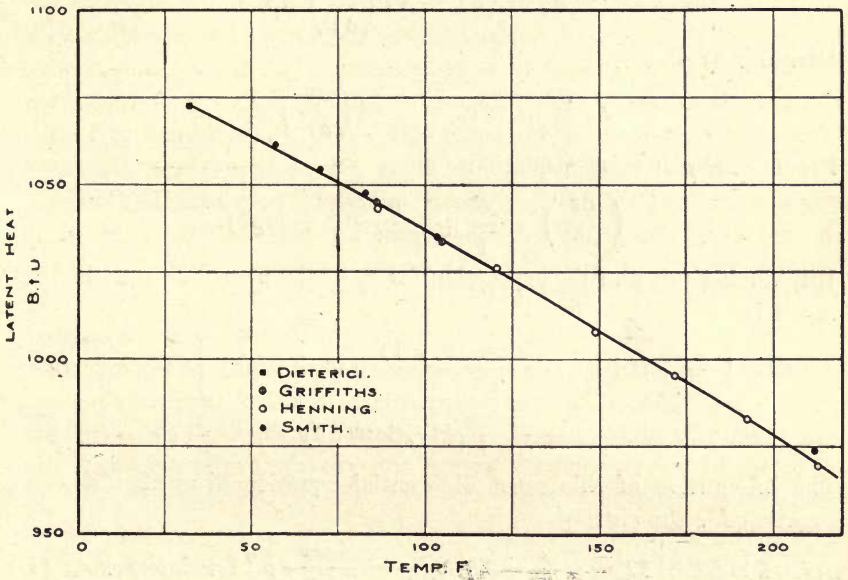

FIG. 14. COMPARISON OF CURVE FOR LATENT HEAT WITH EXPERIMENTAL VALUES.

In Fig. 14 these results are shown by the plotted points and the curve represents the variation of r according to the heat-content equation.

The agreement is satisfactory, though Smith's points would indicate that the calculated values may be slightly low.

Special interest attaches to the value of r at 212° F. For years Regnault's number 966 B. t. u. was universally accepted. Callendar in his 1900 paper had the courage to raise this value to 972, which is almost precisely the value that is now considered most probable. Davis made use of the experiments of Henning and Joly at 212° and set the value of r at 970.4 B. t. u. Smith's recent experiments[1] on slow vaporization of water under atmospheric pressure indicate a value higher than any yet assumed, and Dr. Davis in a communication to the writer expresses the opinion that the number should be at least 972. Heck uses the value 971.2, Mollier uses 971.4. The present investigation leads to the value 971.6, which is probably quite close to the truth, though if anything slightly low.

29. *Entropy.*—An expression for the entropy of superheated steam is readily obtained from the fundamental equation,

$$dq = c_p dT - AT\left(\frac{\partial v}{\partial T}\right)_p dp.$$

Dividing by T,

$$ds = \frac{dq}{T} = c_p \frac{dT}{T} - A\left(\frac{\partial v}{\partial T}\right)_p dp.$$

From the characteristic equation

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{B}{p} + \frac{mn}{T^{n+1}}(1 + 3ap^{\frac{1}{3}}).$$

Introducing this and the expression for c_p in the preceding equation, the result is

$$ds = \left[\frac{a}{T} + \beta + \frac{\gamma}{T^3} + \frac{Amn\ (n+1)}{T^{n+2}}\, p\ (1 + 2ap^{\frac{1}{3}})\right] dT - \frac{AB}{p} dp$$
$$- \frac{Amn}{T^{n+1}}(1 + 3ap^{\frac{1}{3}})\ dp.$$

The integration of this exact differential equation gives the following equation for the entropy

$$s = a \log_e T + \beta T - \tfrac{1}{2}\frac{\gamma}{T^2} - AB \log_e p - \frac{Amn}{T^{n+1}}\, p\ (1 + 2ap^{\frac{1}{3}}) + s_o. \quad \text{(E)}$$

The constant s_o is found by applying the equation at the saturation limit. The value thus determined is $s_o = 0.08085$.

1. Physical Review, Vol. 33, p. 183 (1911).

For the range 32°–212°, within which Callendar's formula for the heat of the liquid is surely applicable, there are available two independent methods of calculating the entropy of saturated steam. 1. The entropy of the liquid s' is determined by the integration of Callendar's equation for i' and the entropy of vaporization $\frac{r}{T}$ is added. 2. Corresponding saturation values of p and T are substituted directly in the preceding formula for s. The two methods should give substantially identical results.

Above 212° the entropy s'' of saturated steam is calculated from formula (E) and the entropy of the liquid s' is obtained by the relation

$$s' = s'' - \frac{r}{T}.$$

Integration of Callendar's i'-equation gives the following formula for s':

$$s' = 2.3623 \log T + 0.0045775 \log (t + 4) - 0.00022609\, T + 0.000\,000\,13867\, T^2 - 6.28787.$$

The following table shows the results of the calculation, the Marks and Davis values being included for comparison.

TABLE 16.

ENTROPY OF LIQUID AND SATURATED VAPOR, 32°–212° F.

Temp. F.	32	40	80	120	160	200	212
s' from Callendar Eq.	0.	0.0163	0.0933	0.1646	0.2312	0.2939	0.3120
$\frac{r}{T}$	2.1823	2.1389	1.9408	1.7692	1.6184	1.4842	1.4467
$s''=s'+\frac{r}{T}$	2.1823	2.1552	2.0341	1.9338	1.8496	1.7781	1.7587
s'' from Eq. (E)	2.1822	2.1550	2.0340	1.9338	1.8497	1.7782	1.7587
Marks & Davis							
s'	0.	0.0162	0.0932	0.1645	0.2311	0.2937	0.3118
$\frac{r}{T}$	2.1832	2.1394	1.9398	1.7674	1.6165	1.4824	1.4447
s''	2.1832	2.1556	2.0330	1.9319	1.8476	1.7761	1.7565

30. *Intrinsic Energy.*—From the defining equation

$$i = A\,(u + pv)$$

the energy u in thermal units is readily obtained by subtraction; thus

$$u = i - Apv$$

Combination of equations (B) and (D) gives therefore the following explicit expression

$$u = (a - AB)\,T + \tfrac{1}{2}\beta T^2 - \frac{\gamma}{T} - \frac{Amnp}{T^n}\left(1 + \frac{2n-1}{n} a p^{\frac{1}{2}}\right) + i_0. \quad \text{(F)}$$

E. JOULE-THOMSON EFFECT.

31. *The Joule-Thomson Coefficient.*—The ratio of the drop in temperature to the decrease of pressure when a fluid is subjected to a throttling process is the Joule-Thomson coefficient μ. Since in such a process the heat content i is constant, the value of μ is given by the derivative $\frac{dT}{dp}$ evaluated under the condition that i is constant; that is

$$\mu = \left(\frac{dT}{dp}\right)_{i = \text{const.}}$$

It follows, therefore, that the slope of a throttling curve (See Fig. 9) at any point is the value of μ at that point.

An expression for μ is readily derived from the equation for heat content,

$$i = aT + \frac{1}{2}\beta T^2 - \frac{\gamma}{T} - \frac{Am(n+1)}{T^n}\, p\,(1 + 2ap^{\frac{1}{2}}) + Acp + i_0.$$

With i constant

$$\left(\frac{dT}{dp}\right)_i = -\left(\frac{\partial i}{\partial p}\right)_T \div \left(\frac{\partial i}{\partial T}\right)_p.$$

But

$$\left(\frac{\partial i}{\partial T}\right)_p = c_p,$$

hence

$$\mu = \frac{A}{c_p}\left[\frac{m\,(n+1)}{T^n}(1 + 3ap^{\frac{1}{2}}) - c\right] \qquad (G)$$

32. *Comparison with the Throttling Experiments.*—From the four available sets of throttling experiments, Davis[1] has computed values of μ covering a wide range of pressure and temperature. As might be expected, the results when plotted showed a broad band of points (See Fig. 6 of Davis' paper) and individual measurements showed considerabl discrepancy. By passing a smooth curve through the band of points Davis obtained the relation between μ and t that was afterwards used by himself in spacing the specific heat curves, and by Heck in the development of his theory. Davis therefore assumes that μ is a function of the temperature only, while according to the preceding equation (G) μ must vary with the pressure also.

A comparison of equation (G) with the values of μ computed by Davis is shown in Fig. 15. Four different pressures are used, 36, 120, 200, and 300 lb. per sq. in., and the points are plotted from the data

1. Proc. Am. Acad., Vol. 45, pp. 243-264.

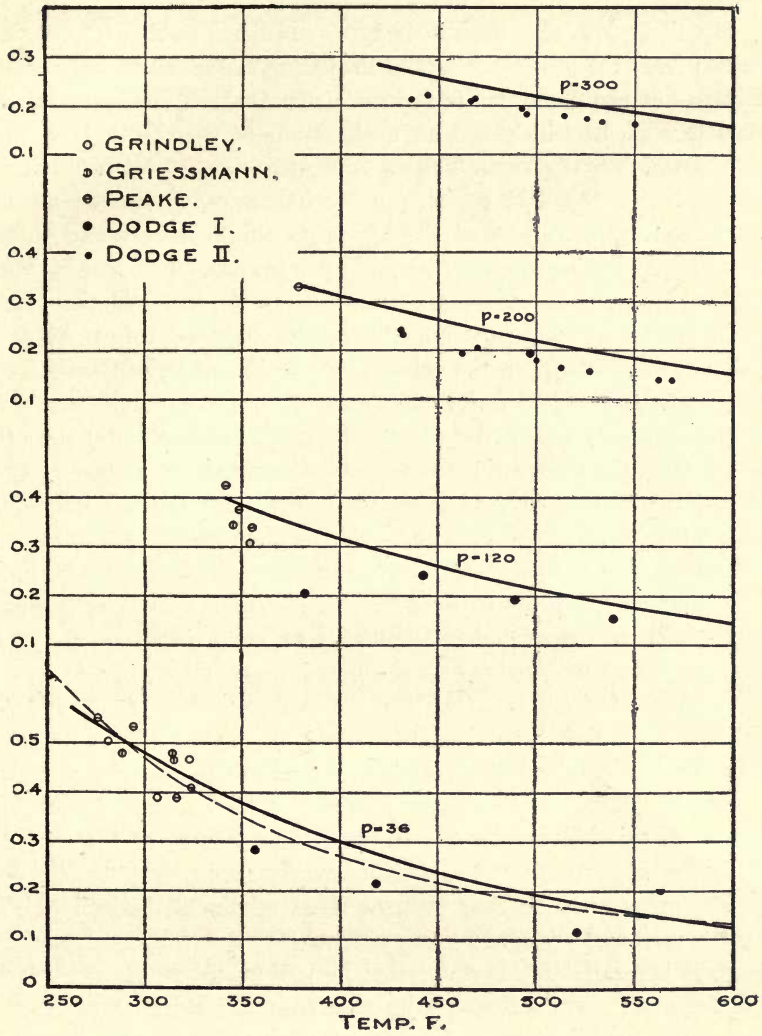

FIG. 15. JOULE-THOMSON COEFFICIENT.

given in the tables of Davis' paper. The points in each group are so chosen that the pressure in the experiments represented by them is very nearly the pressure attached to the corresponding curve. The dash curve through the lowest group is the Davis curve for μ.

It will be seen that the curves agree sufficiently well with the points obtained from the first three sets of throttling experiments, but that they lie somewhat above the points deduced from Dodge's experiments. Reference to Fig. 10 will afford an explanation of the discrepancy in the case of Dodge's first series. The peculiar discontinuity between the high-side point and the first low-side point has already received comment (See p. 47). Davis rejected the high-side point entirely and obtained values of μ by a comparison of low-side points only. This was equivalent to taking the slopes of smooth curves running through the low-side points, and it is evident from the figure that the values of μ thus obtained are smaller than the values given by the slopes of the theoretical curves. Dodge's second series of 33 experiments was of such a character that the high-side observations had to be used. The values of μ obtained directly from the observations were, according to Davis, abnormally high, and certain corrections were made to reduce them to the level required by the law of corresponding states. The chief correction was a reduction of the high-side temperature by an amount ranging from 11° to 14°. If the high-side points are incorrect, as assumed by Davis, because of water carried in suspension in the highly superheated steam, the plotted points representing Dodge's experiments must be accepted, and the curves obtained from eq. (G) run somewhat high. If, on the other hand, the error lies in the low-side points, the values of μ calculated by Davis are too low, and the curves probably are nearer the truth than the points. The question can only be settled by a new series of experiments with suitable precautions to insure the dryness of the steam and with improved methods of temperature measurement.

The other question that presents itself relates to the variation of μ with the pressure. According to equation (G) this variation must exist, though it is small. Davis states that he was unable to detect such variation from an examination of the observations. Heck assumed at the start of his investigation that μ depended on t alone, but the further development of the theory led him to the conclusion that the assumption could not be rigorously correct. It is apparently impossible to construct a general theory that will give satisfactory agreement in other parts of the field and at the same time leave the coefficient μ unaffected by the

pressure. We conclude, therefore, that μ *is* a function of the pressure; and so far as our present knowledge extends, the value of μ is given satisfactorily by equation (G).

F. THERMAL PROPERTIES NEAR THE CRITICAL TEMPERATURE.

33. *Previous Investigations.*—That the equation (B) to (F) (at the saturation limit) should hold good up to the critical temperature is not to be expected. In the vicinity of the critical point the variation of some of the thermal properties is so rapid that to represent these properties, equations of a different form must be used. As there are no trustworthy experiments in the range 600° F. to the critical temperature, any formulation covering this region must be regarded as a guess. However, even a conjecture may have a qualitative value, and in the present case the investigation at least serves to establish quite closely the upper limit of temperature for the equations developed in the preceding sections.

Several attacks have been made on this problem. Davis[1] by the use of Thiesen's exponential formula determined the latent heat r, and by "the law of the straight diameter" established tentatively the specific volume v''. Schüle[2] has likewise estimated certain of the thermal properties near the critical temperature, and his work appears to have a reasonable basis. Another tabulation was published in *Engineering* (Jan. 4, 1907); this is palpably incorrect and has no value whatever.

34. *Thiesen's Exponential Formula.*—At the critical temperature, the latent heat r becomes zero, and furthermore $\frac{dr}{dt} = -\infty$. An equation connecting r and t may be given a form such that these conditions will be satisfied. The simplest form is that suggested by Thiesen, namely.

$$r = C\,(t_k - t)^n,$$

in which t_k denotes the critical temperature, and $n < 1$. If now the constants can be so determined as to give correct values of r at ordinary temperatures, then it may be inferred that the formula will give reasonably good values for higher temperatures. The formula may be written

$$\log r = \log C + n \log (t_k - t)$$

a form more convenient for purposes of calculation.

Davis[3] found that with $\log C = 2.14302$, $n = 0.315$, and $t_k = 689$, the formula represented the available experimental values of r with remarkable accuracy. The number 689 is however the older value of

1. Marks and Davis Steam Tables, pp. 102-105.
2. Zeit. des Verein. deutsch. Ing., Vol. 55, pp. 1561-1567 (1911).
3. Proc. Am. Acad., Vol. 45, p. 284.

t_k due to Cailletet and Colardeau. The recent experiments of Holborn and Baumann[1] raise the value of t_k to 706.3° F., and with this value it appears to be impossible to make Thiesen's formula fit any series of probable values of r through a wide range of temperature. It is found, however, that the equation

$$\log r = 2.00117 + 0.3685\ (706.3 - t)$$

fits reasonably well the values of r from 360° to 560°. The following table shows the agreement.

TABLE 17.

COMPARISON OF VALUES OF LATENT HEAT.

Temp. F.	360	400	440	480	520	560	600
r deduced from Eq. (D)	863.5	826.7	785.5	739.6	688.0	629.6	563.1
r from Thiesen's Eq.....	864.9	826.6	785.1	739.4	688.2	629.6	559.7

Below 360° and above 560° the two sets of values diverge rapidly. It is assumed that the formula will give approximate values of r between 560° and 706.3°, but too much confidence should not be placed in the accuracy of the results thus obtained.

35. *Heat Content of Liquid and Vapor.*—The law of the mean diameter has frequently been applied in determining the specific volume of the vapor. A somewhat similar application is here made in connection with the heat contents i' and i''. Taking the sum $i' + i''$ for the temperature range 400°–600° F., it is found that this sum is given very accurately by the equation

$$i' + i'' = 956.94 + 1.923t - 0.00095t^2.$$

It is assumed that this relation also holds good from 600° to the critical temperature. Hence with the sum $i' + i''$ determined by this equation and the difference $i'' - i' = r$ determined from the Thiesen exponential equation, values of i'' and i' are readily calculated. The variation of these thermal magnitudes near the critical temperature is shown in Fig. 16. Curve CD is the mean diameter, its ordinate being $\frac{1}{2}(i' + i'')$, curve AD represents the heat content i'' of the vapor, and curve BD the heat content i' of the water. These are two branches of a continuous curve, and the common value of i' and i'' at the critical temperature is apparently about 921 B. t. u.

36. *Specific Volume of Steam.*—The method of Davis[2] has been followed, except that 706.3 is used for the critical temperature. Values of v'' the specific volume of steam were calculated from the characteristic

1. Annalen der Physik, Vol. 31, pp. 945-970 (1910).
2. Steam Tables and Diagrams, pp. 103-105.

equation (B). For the values of v', the specific volume of water, the formula of Avernarius

$$v' = a - b \log (t_k - t)$$

was found to give exact results for the temperature range 280° — 600° F., with the following constants: $a = 0.044825$, $b = 0.0105$. Denoting by $2s$ the sum of the densities of the liquid and vapor, that is

$$2s = \frac{1}{v'} + \frac{1}{v''}$$

the variation of this sum with the temperature is given by the equation

$$2s = 67.1 - 0.029131\, t - 0.000009342\, t^2.$$

The Clapeyron relation gives another relation connecting v' and v'', namely

$$r = A\,(v'' - v')\,T\frac{dp}{dT}.$$

in which the derivative $\frac{dp}{dT}$ is found from eq. (A) and r from the Thiesen formula. The values of v'' and v' are therefore readily obtained by the solution of a quadratic equation.

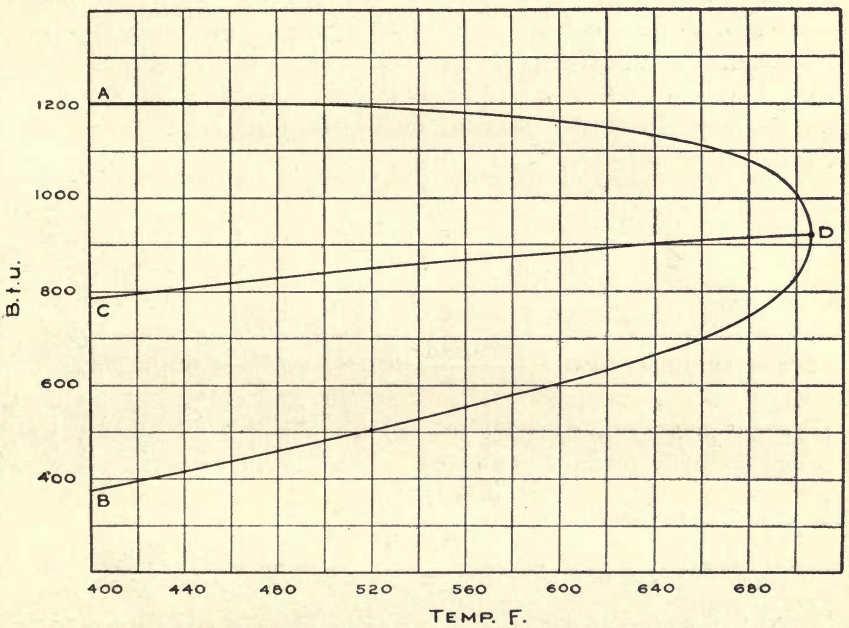

FIG. 16. CURVES FOR i' AND i" FROM 400°-706.3° F.

37. *Table of Properties at High Temperatures.*—The following table gives the thermal properties of saturated steam between 600° and the critical temperature, as calculated by the methods just described. It is to be understood that the tabulation is merely a conjecture and that no claim of extreme accuracy is asserted.

TABLE 18.

PROPERTIES OF SATURATED STEAM FROM 600° TO 706.3° F.

Temp. F.	Pressure: lb. per sq. in.	Volume of 1 lb.	Weight of 1 cu. ft.	Heat Content		Latent heat
				of liquid	of vapor	
600	1540.4	0.272	3.68	604.5	1164	560
620	1658.7	0.241	4.15	633	1151	518
640	2056.6	0.187	5.35	663	1136	473
660	2360.8	0.151	6.63	700	1112	412
680	2699.1	0.118	9.86	745	1080	335
700	3074.5	0.080	12.46	823	1016	193
706.3	3200	0.048	20.92	921	921	0

Comparing the equations used in deducing the values in this table with the original equations (B) and (D), it is found that the former merge into the latter at a temperature lying between 560° and 600° F. The discrepancy at 600° is small. It may be reasonably assumed, therefore, that the general equations developed in this investigation hold good up to 600° F. when applied to the saturated vapor. The corresponding pressure limit is above 1500 lb. per sq. in.

V. RESUMÉ OF FORMULAS.

For convenience of reference the principal formulas developed in the preceding section are here collected. The constants are for English units with pressures expressed in pounds per square *inch*. The logarithms involved are common logarithms.

1. Relation between pressure and temperature:

$$\log p = 10.5688080 - \frac{4876.643}{T} - 0.0155 \log T - 0.00406258\, T$$

$$+ 0.00000400555 T^2 - 0.00002\left[10 - 10\left(\frac{t-370}{100}\right)^2 + \left(\frac{t-370}{100}\right)^4\right] \quad \text{(A)}$$

$$T = t + 459.6$$

2. For the specific volume:

$$v - c = 0.59465\frac{T}{p} - (1 + 0.05129 p^{1/4})\frac{C_1}{T^4} \qquad \text{(B)}$$

in which $\log C_1 = 10.82500$, and c may be given a mean value 0.017.

3. For the specific heat:

$$c_p = 0.320 + 0.000126T + \frac{23583}{T^2} + \frac{C_2 p\,(1 + 0.0342 p^{1/2})}{T^5} \qquad (C)$$

$$\log C_2 = 11.39361.$$

4. For the heat content:

$$i = 0.320T + 0.000063T^2 - \frac{23583}{T} - \frac{C_3 p\,(1 + 0.0342 p^{1/2})}{T^4} + 0.00333p + 948.7 \qquad (D)$$

$$\log C_3 = 10.79155.$$

5. For the entropy of superheated steam

$$s = 0.73683 \log T + 0.000126T - \frac{11791.5}{T^2} - 0.25355 \log p - \frac{C_4 p\,(1 + 0.0342p)}{T^5} - 0.08085 \qquad (E)$$

$$\log C_4 = 10.69464$$

6. For the intrinsic energy of superheated steam, in B. t. u.:

$$u = 0.2099T + 0.000063T^2 - \frac{23583}{T} - \frac{C_5 p\,(1 + 0.02992 p^{1/2})}{T^4} + 948.7 \qquad (F)$$

$$\log C_5 = 10.69464$$

7. Heat of the liquid between 32° and 212° from Callendar's formula:

$$i' = 0.9838t + 2.0856 \log (t + 4) + 0.233 \left(\frac{t - 32}{100}\right)^2 + 0.09245 \left(\frac{t - 32}{100}\right)^3 - 34.73.$$

8. Entropy of the liquid between 32° and 212°, from Callendar's formula

$$s' = 2.3623 \log T + 0.0045775 \log (t + 4) - 0.00022609\,T + 0.00000012867T^2 - 6.2879.$$

9. External latent heat of saturated steam:

$$\psi = 0.1101\,T - \frac{C_6 p\,(1 + 0.05129p)}{T^4}$$

$$\log C_6 = 10.09258.$$

10. Latent heat of saturated steam:

$$r = \psi \frac{T}{p} \frac{dp}{dT}$$

in which $\frac{T}{p} \frac{dp}{dT}$ is derived from formula (A).

The preceding equations are sufficient for the calculation of all the thermal properties of saturated and superheated steam that are usually found in steam tables.

VI. Conclusion.

38. *Comparison of Tables and Formulations.*—A table of the properties of steam, or a formulation from which a table may be calculated, should possess two characteristics, *consistency* and *accuracy*. A table or formulation is consistent when the values are obtained from equations that are properly connected by thermodynamic relations, such as the Clausius and Clapeyron relations. It may be considered accurate if the calculated values show close agreement with the most reliable experimental data. In this sense, accuracy is only relative. A table that would have been considered accurate ten years ago would be regarded today as extremely inaccurate in the light of our present knowledge of the subject.

Taking these two characteristics as a basis of classification, the existing tables and formulations may be divided into four groups:

1. Those that possess neither consistency nor accuracy.
2. Those that are consistent but inaccurate.
3. Those that are reasonably accurate but lack consistency.
4. Those that are both consistent and accurate.

In the first group may be placed all the older tables, such as Rankine's, Buel's, Porter's, and Dery's. The tabular values were calculated from empirical formulas based chiefly on Regnault's data, and the necessary connection through thermodynamic relations was not recognized.

In the second group are the tables based on Callendar's theory. As regards consistency these tables are entirely satisfactory, as the thermodynamic relations are satisfied. Mollier's tables appeared before the publication of the decisive Munich experiments, which invalidated some of the fundamental assumptions of Callendar's theory. Smith and Warren, however, have apparently ignored completely the mass of experimental evidence accumulated since 1900, and have deliberately sacrificed accuracy for the sake of consistency. While these two sets of tables are probably more accurate than those in the first group, they are nevertheless grossly inaccurate according to present standards.

The noteworthy researches of Davis have been embodied in the Marks and Davis steam tables and in the last edition of Peabody's tables. The establishment of the new formula for the heat content of saturated steam was the principal achievement of Dr. Davis, and the incorporation of this formula in the tables marks an important advance in accuracy. The Marks and Davis tables are not rigorously consistent, and in some particulars they also exhibit a lack of extreme accuracy. The system of

specific heat curves used as the basis of the values in the region of superheat is probably somewhat in error, as noted in a preceding section. The values of the specific volume of superheated steam are probably too high, and the values of the heat content in the region of superheat are almost certainly too low (See Fig. 11). The value 970.4 B. t. u. assumed for the latent heat at 212° F. is doubtless slightly low. Notwithstanding minor defects in accuracy and consistency, the Marks and Davis tables are justly held in high regard, and they have been very generally accepted as standard in engineering practice.

In the fourth group may be included the formulations of Jakob and Heck, and the formulation developed in the preceding sections. In each of these, consistency is secured by a strict observance of thermodynamic relations; at the same time the available experimental data are used to check the equations, and thus a high degree of accuracy is insured. It is probable that a table derived from any one of these formulations would surpass in accuracy the best of existing tables.

With respect to the relative advantages of the three formulations, the following statements may be made. Jakob's scheme is open to the objection that it is graphical. Numerical results must be obtained by measurement of geometrical magnitudes. Furthermore, Jakob's system of specific heat curves, like Davis' system, is probably erroneous near the saturation limit. For these reasons Jakob's formulation may be considered the least satisfactory of the three. Heck's theory doubtless shows good agreement with experimental data, and a table constructed from it should be thoroughly satisfactory as regards accuracy and consistency. In the few cases in which comparisons have been made, the theory described in this bulletin appears to show somewhat closer agreement with experimental data than Heck's theory. Equation (A) for the pressure-temperature relation is evidently superior to Heck's modification of Marks' formula; the characteristic equation (B) represents the Knoblauch measurements more accurately than Heck's equation; and equation (D) for the heat content gives values of i at saturation that agree very closely with the points deduced by Davis from the throttling experiments, while Heck's curve for i runs appreciably higher.

As regards accuracy, the theory under discussion does not suffer in comparison with Heck's theory. In other respects it presents certain obvious advantages. (1) The range within which the formulation may be regarded as valid is somewhat greater. At saturation Heck's equations

hold good up to 500° F., or perhaps a little higher; the equations (B) to (F) are valid up to nearly 600° F. (2) Heck's equations are excessively complicated and ill-adapted for computation. Equations (B) to (F) are in comparison relatively simple, and because of the repetition of certain terms in the several formulas the labor of computation is greatly abridged, and numerical results may be obtained with comparative ease.

39. *Effect of Future Experiments.*—The theory under discussion has been correlated with the most reliable experimental data available at the present time. It is, of course, probable that subsequent experiments of a higher order of precision will modify these data to some extent and possibly render necessary a revision of the formulation. It may be profitable in this connection to discuss briefly the sufficiency of existing data and indicate the possible effect of future experiments.

The pressure-temperature determinations may be regarded as final. It is not likely that further experiments will modify these to any extent. Further experiments on specific volumes are desirable; these should include a higher superheat and much greater pressure range than the Munich experiments. Such experiments would probably confirm the results of Knoblauch, Linde, and Klebe. The results of the experiments of Lanz and Schmidt on the specific heat of steam at the higher pressures are awaited with interest. A preliminary report indicates that the experiments of Knoblauch and Mollier are substantially confirmed. The experiments at higher pressures should settle the question of the proper course of the specific heat curves near the saturation limit. With reference to the specific heat of water, the results of Barnes and Callendar for the range 32°–212° should be accepted. For the range above 212° the experimental evidence is at present unsatisfactory and further experiments in this field are urgently needed. Finally, the questions raised by the various discrepancies in the throttling experiments should be settled by a new set of experiments conducted with proper precautions to insure the dryness of the steam and the accuracy of the measurements.

While the theory may require modification as additional experimental data become available, it is believed that such modifications as may be necessary can be made without essential changes in structure. The formulation is extremely sensitive to changes in the constants and any modifications that are likely to be made in the fundamental data, volumes, specific heats, etc., can be accommodated by slight changes in the constants.

40. *Summary.*—In this bulletin is described the development of a general theory of the properties of superheated and saturated steam. For this theory the following claims are urged.

1. *Consistency.*—In the deduction of the fundamental equations the thermodynamic relations have been recognized, and the satisfaction of these relations assures consistency.

2. *Accuracy.*—The equations have been checked with the most reliable experimental data available, and in every respect the agreement is extremely close. It may be asserted that the formulation is at least as accurate as any other that has thus far appeared.

3. *Simplicity.*—The equations are relatively simple and well adapted for computation of numerical results.

4. *Flexibility.*—The structure of the formulation is such that modifications necessitated by further experimental data can probably be made by slight changes of the constants.

5. *Range of Validity.*—At the saturation limit the equations are valid throughout the range 32°–600° F., a range far wider than is at present employed in engineering practice.

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Circular No. 1. High Speed Tool Steels, by L. P. Breckenridge. 1905. *None available.*

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